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Colloidal Aspects of the Dyeing of Wool With Acid Dyes

By HERMAN BOXSER

Explanations for phenomena produced in the application of dyestuffs to textile fibers even to the present advancement of scientific knowledge still remain in the hypothetical stages. At present we do not have one accepted theory of dyeing which covers the coloring of all textile fibers. That dyeing is a phenomenon in which there occurs a true chemical interreaction between the dye and fiber appears to be a theory favored by many for the application of acid dyes to wool. However, this theory of a chemical interreaction finds a weak foundation when the application of substantive dyes to cotton is considered.

THE colloid chemist has formulated a theory relative to the substantive dyeing of cellulose, the essence of which has been expressed by Briggs, (Jour. Phys. Chem. 28, 368, 1924). "Dyeing with substantive dyes is simply a case of adsorbing from suspension a colloid, the degree of dispersion and stability of which are capable of considerable variation." "Adsorbing" in this explanation implies the unequal distribution of a substance at the boundary of two heterogeneous phases, (Taylor, Chemistry of Colloids, Longman Green 1923, P. 247).

There has been much work accomplished by such investigators as Mark (Melliand 1, 1, 1929), Clark, (Ind. and Eng. Chem. 22, 5, 1930). Hibbert (14, 1, 1925) and Bragg (Cellulose 1, 4, 1930) on the structure of cellulose, which has aided the propounding of a sounder theory of dyeing cellulose.

Researches on the micelle structure of wool have not been numerous, and that which has been recently accomplished has originated to the greatest extent from England.

In the present article the writer will attempt to discuss the application of acid dyes to wool from a colloidal standpoint, especially as regards the action of acid dyes which exhibit neutral dyeing properties. Before describing the action of acid dyes in solution it would be well to gain some insight as to the make-up of the wool fiber itself.

According to Matthews (Textile Fibers, Wiley, P. 76, 1924) wool consists of several distinct portions:

(a) A cellular marrow containing pigment matter to which wool owes its color.

(b) A layer of cellular fibrous substance or cortical tissue which gives the wool its strength and elasticity.

(c) An outer layer or epidermis consisting of flattened cells or scales the ends of which overlap each other and project outward causing the fiber to present a serated appearance. These scales are responsible for the rigidity and resistance of the fiber. Bowman (Structure of Wool Fiber, Macmillan, P. 103, 1908), describes the structure of wool as cellular with the innermost cells of greater diameter than the outer ones, the latter being superimposed by a scaly surface. In discussing the cortex or cortical tissue Bowman describes this as a continuous membrane capable of permitting the passage of liquids through it, thus acting like a dialyser.

The resemblance of the structure of wool to those of colloidal gels has been emphasized by J. B. Speakman (Jour. Text. Inst., 17, T457, 1926). It had been the opinion of previous investigators that the wool fiber possessed a two phase gel structure, namely, a fibrillar structure which enclosed a viscous medium, one in physical equilibrium with the other. Speakman, however, found that wool fiber consisted of two gels arranged in parallel. The first gel might be called a petrified gel and comprises an elastic cell wall which encloses a fibrillar structure which is *not* in physical equilibrium with a viscous

phase. The second gel fills the interstices of the above mentioned petrified gel and is capable of reversible solution in, or deposition from water. The gel structure of wool according to Speakman may be described as:

(1) An enclosing elastic cell wall.

(2) A fibrillar structure which is not in physical equilibrium with

(3) A biscous medium of gelatinous character included in its interstices.

On noting the property of wool of slow retraction following its subjection to tension, a characteristic displayed by gels, Shorter, (Jour. Text. Inst. 15, T207, 1924) concluded that the wool fiber consisted of three sets of elements.

(1) Elastic elements which extend and contract freely coupled to

(2) Elastic elements which are impeded in their extension and contraction by

(3) Elements which act as a resistant medium.

Most recent researches tend to emphasize the micelle structure of wool. At present when cellulose is mentioned, we visualize this fiber as composed of micelles or large crystallites to which cellulose owes its chemical and dyeing properties. If a micelle structure of wool is clearly demonstrated we may then regard the wool fiber as somewhat analogous to cellulose in regards to the adsorption theory of dyeing. Asbury (Jour. Text. Science, 1, 28, 1931) in executing x-ray investigations of the inner structures of wool found a distinct crystalline pattern, stating that the elements of wool fibre are shown to be built up in a regular 3-dimensional pattern. The crystals are minute and their aggregation is colloidal. X-ray photographs showed that stretched and unstretched wool have different crystallographic structures, the difference being ascribed to the possible presence of a Beta and an Alpha keratin.

Speakman (Nature 126, 565, 1930) in reviewing one of his most recent papers on investigations conducted on the micelle structure of wool (Trans. Faraday Soc. 26, 61, 1930) stated that the size of the capillary spaces in dry wool fiber is of the same order as the length of the n-propyl alcohol molecule. On observing the extensibility of wool in various liquids, Speakman found that the wool fiber extended greatest in water, and also to a great extent in methyl alcohol and ethylene glycol. However, its extensibility in higher alcohols, (butyl and amyl) was not so great. In these experiments, Speakman after noting a large increase in the pore size of the wool but not in cross-sectional area, assumed the existence within the fiber of certain micelles which are relatively impervious to molecules as small as the H_2O molecule. By determining the critical point at which octyl alcohol was admitted by a known amount of Methyl alcohol the thickness of the micelle was determined. It was found to be 200 Angstrom units.

Instead of being a simple molecular body to which a definite formula might be given, wool is composed of several chemically distinct substances. The principal component of the fibre is a protein, keratin, whose composition is approximately as follows:—

Carbon	50%
Hydrogen	7%
Oxygen	26-22%
Nitrogen	15-17%
Sulphur	2-4%

This compound differs from other proteins in the large proportion of sulphur present, much of which appears to be in a state of loose combination. S. R. and E. R. Trotman and R. W. Sutton (Jour. Soc. Chem. Ind. 45, 30, 1926) claim that sulphur, however is not a structural constituent of wool fiber.

In the foregoing we have considered three conceptions of the structure of the wool fiber, (1) Cellular, (2) Gel and (3) Micelle. Since either of these conceptions might be conceived in terms of the other we may conclude that these infer a colloidal structure of the fiber. Assuming that wool possesses a micellar structure not unlike cellulose, we may then regard the phenomenon of dyeing with acid dyes as one favoring adsorption.

Theory of Acid Dyeing

Acid dyes are sodium or calcium salts of sulphonic acid derivatives. They are applied to wool either from an acid or neutral bath, the manner of application depending on the properties of the respective dyestuffs. The function of the acid is to liberate the free color-acid from the dyestuff, which combines with the fiber-base. Matthews (Application of Dyestuffs, Wiley, P. 594, 1920) represents this interreaction in the following manner:—

[Color Acid: Soda] + H_2 SO_4 → [Color Acid: Hydrogen] + Na_2 SO_4 Dyestuff Salt + Sulphuric Acid → Free color acid + Sodium Sulphate Color acid + Wool base → color lake.

Hummel (Thorpe's Dictionary of Applied Chemistry Vol. I P. 702) also states, as in the above illustration, that wool acts like a base with dyes of marked acid character, like sulphonic acid azo dyes.

The principal assistant employed in acid dyeing is Glauber's Salt, which acts as a retarding agent. Matthews (Supra) explains the retarding action of Glauber's Salt in terms of the graphical equation presented above. As Glauber's Salt (Sodium Sulphate) is a product of the interreaction between the dye salt and acid, its excess presence will retard this reaction, since it is a principle of chemistry that when one of the products of a chemical reaction is present in the solution, the rapidity and extent of the reaction will be reduced.

Thus in the preceding few paragraphs we have a purely chemical explanation,—i.e., one of chemical interreaction for the action of acid dyes on wool. The colloid chemist, however, has advanced a theory which regards the acid dyeing of wool as a colloidal phenomenon, depending on the theory of adsorption. This has been conceived by W. D. Bancroft (Jour. of Phys. Chem. 18, 2, 1914) who denies the existence of a chemical reaction between the

(Continued on page 99)

Proceedings of the American Association of Textile Chemists and Colorists

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CALENDAR OF COMING EVENTS

* * *

Meeting Northern N. E. Section, Feb. 6th.

* * *

Meeting Southeastern Section, Feb. 6th.

ANNUAL MEETING OF PIEDMONT SECTION

THE Annual Meeting of the Piedmont Section was called to order by the Chairman, Samuel L. Hayes, following a very delightful dinner and entertainment program.

Reports of the Secretary and Treasurer were accepted as read. Reports also were submitted by Chairman of the Membership Committee, Mr. Hugh Pucket, and Professor A. H. Grimshaw, Councilor of the Junior Section at North Carolina State College.

The nominating committee presented the following names for the 1931-32 offices: Chairman, John L. Crist, Charlotte; Vice-Chairman, A. R. Thompson, Jr., Salisbury; Secretary, J. D. Sandridge, Greensboro; Treasurer, re-elected, G. P. Feindel, Greenville, S. C. The above officers were unanimously elected.

A paper was read by Paul F. Haddock on "Purchasing Products and Selling Results." Mr. Haddock's paper accompanies this report. (See page (72) 92.)

Mr. F. Sterling Wilson, Chief of the Business Research Section of the Marketing Service Division of the United States Department of Commerce, made an address on "Some Commercial Aspects of the Textile Industry."

The attendance was 160.

Respectfully submitted,
A. R. Thompson, Jr., *Secretary.*

ELEVENTH ANNUAL MEETING CONTINUED

Note: Other reports of the Annual Meeting appeared in the Jan. 4th and 18th issues of the Reporter.

Saturday Afternoon Session

December 5, 1931

The meeting convened at two-twenty o'clock, Dr. E. H. Killheffer presiding.

Chairman Killheffer: Your President, Mr. Wood, had a little operation not a very long time ago and he isn't feeling just as strong as he should so he asked me if I would come up here for a little while this afternoon and take his place. So I will do the best I can.

I am sure we are all very much pleased that we are to be privileged to listen to Professor Bancroft. Whatever he says is always very much worth while listening to so I won't waste any more time and will introduce to you Professor Bancroft who will talk to you on "Basic Mordants and Lakes."

Proceedings of the American Association of Textile Chemists and Colorists

Basic Mordants and Lakes*

By **PROF. WILDER D. BANCROFT**
Cornell University

MR. CHAIRMAN, Ladies and Gentlemen: I am not going to introduce new definitions at all. I am going to start with the statement that a mordant is a substance that is adsorbed strongly by the fiber and will then take up the dye strongly. Today I am interested primarily in the basic mordants, the hydoxides of aluminum, iron, chromium, tin, copper, and zinc.

When a dye is taken up by a mordant in the absence of a fiber, the product is called a lake. We also use the term lakes in certain other cases where we really have dyed salts. Lakes on a barium sulphate base are a case in point.

As you know, there has been no end of question as to whether the lakes or the mordant and the dye are compounds. You will find the literature full of hypothetical alumina alizarin lakes and what the chemists will do in that way is surprising. I know of a case where a man took calcium, alizarin, and alumina in certain molecular proportions; he put them together and the whole thing precipitated. He analyzed the precipitate and found that they came out in exactly the same molecular proportions as he started with. Of course they did, because the whole thing precipitated.

Another man didn't want the same compound so he took the constituents in another set of ratios which he knew would precipitate completely and his analysis was as good as his synthesis and that was practically all there was to it.

Weiser, at Rice Institute, has been doing a certain number of experiments recently which clear the thing up. With the phase rule method we can answer the question definitely. If we plot the varying concentration in the solution against the varying amount of the dye taken up by the fiber or the mordant, we shall get a smooth curve (A in Fig. 1), if we are dealing with adsorption. If, on the other hand, we have a definite chemical compound formed, there will be flats in the curve (B in Fig. 1). At first there won't be anything taken up; then the compound will start to form and the concentration will remain practically constant until the whole of the material is converted into the compound. It is as simple as that. It isn't a question of whether I think it is a compound or an adsorption or whether you think it is a compound or an adsorption. You can prove the thing, and Weiser has shown that with chromic oxide and sulphate he got a perfectly smooth adsorption of sulphate with a varying pH. That is, under the conditions with which he was working, there was absolutely no formation, for instance, of a basic chromic sulphate. The sulphate was adsorbed and that is all there was about it. With Orange II, he got exactly the same sort of thing. With Methylene Blue, working over on the alkaline side, he also got a smooth curve.

Then working with Alizarine SW, which I think is a monosulphonate, he also got with alumina or chromium oxide, under those conditions, a continuously varying adsorption with varying pH. He didn't do the experiment with a varying concentration at constant pH, but undoubtedly the results would have been more or less similar. If the different samples of the mordant are not aged to the same extent, there is a possibility of error; but there should be no difficulty in correcting for this.

There are some data that seem to contradict Weiser's conclusions. Reinmuth and Gordon at the Johns Hopkins University have published some work to show that with Orange II and alumina they got a perfectly definite chemical compound. They said they varied the concentration but really they only thought they did. Of course, when you boil for three hours, it is possible that a definite stoichiometric compound is formed; but I don't know of any case of dyeing with alumina mordant where you boil for three hours and I am inclined to think that those experiments where they didn't do that are in error. We are going to check those as soon as we can. We haven't had time to do that.

If we treat an alumina alizarin lake with a small amount of caustic soda it takes up the alkali to form sodium alizarate in which case the lake cannot also be aluminum alizarate. That seems to have been overlooked by the people who write about lakes as compounds. There is an interesting point about this. The lake is the same red color in presence of alkali or of acid, although solid sodium alizarate in purplish and free alizarinic acid is brownish-yellow. At first sight the answer seems to be that we have in both cases a red aluminum alizarate and that the caustic soda is only adsorbed.

That is not the right explanation and Weiser has solved the problem. If alumina is an ionizing adsorbent, we shall not have sold aluminum alizarin or solid alizarinic acid. We shall have alizarin ion in both cases, which ac-

*Paper presented at Annual Meeting, Boston.

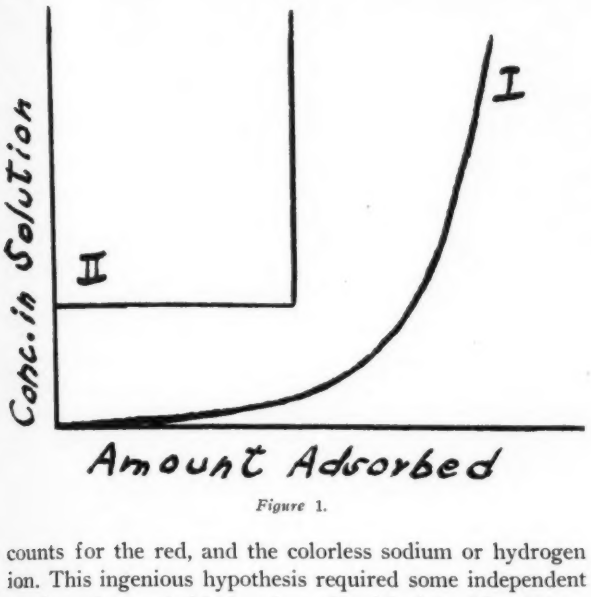

Figure 1.

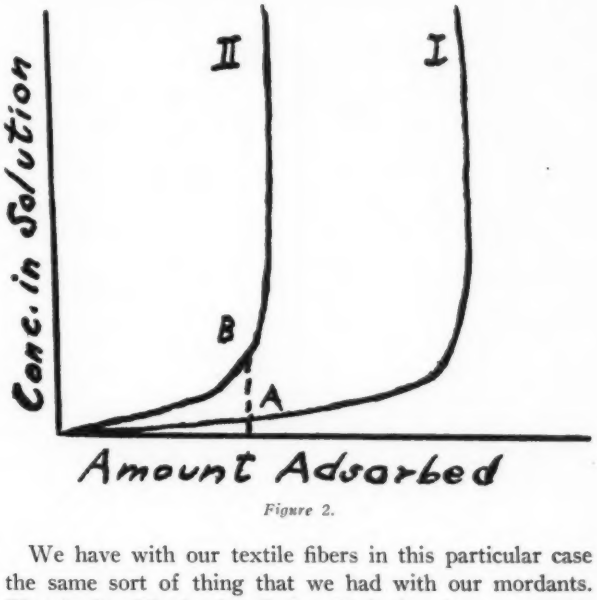

Figure 2.

counts for the red, and the colorless sodium or hydrogen ion. This ingenious hypothesis required some independent confirmation and this has been furnished by Mr. Ackerman and myself.

It seemed possible that there might be other mordants which did not ionize the adsorbed material to the same extent. If so, we should get a color approaching that of solid sodium alizarate in presence of alkali and approaching that of solid alizarinic acid in presence of acid. We found this in hydrous stannic oxide. A tin lake is definitely purple in presence of alkali and definitely orange-yellow in presence of acid. Hydrous zinc oxide does not take up much alizarin; but the lake is pale purple in presence of alkali and pale yellow in presence of acid. In other words, alumina is a strongly ionizing adsorbent for alizarin, stannic oxide is a weakly ionizing adsorbent, and zinc oxide is practically non-ionizing adsorbent. Incidentally, this accounts for alizarin being called a polygenetic dye. We get different colors because the alizarin is in different states.

It now occurred to us that we could point out the flaw in Witt's theory of solid solution in dyeing. Rhodamine doesn't fluoresce when solid. It does fluoresce in solution. It fluoresces on silk. Therefore, Witt said that it must be in solution. It must be a solid solution.

Of course, he didn't mention the fact that it doesn't fluoresce on cotton and not much on wool. It was possible to explain everything, if silk, wool and cotton were adsorbents with varying ionizing powers.

We took Rhodamine G because that has the nicest fluorescence of any of them that I know of. It dyes silk, wool and cotton, all more or less of a yellow red. On silk there is a strong yellow fluorescence. On wool there is a negligible fluorescence. You have got to do some very careful measurements to be sure that it does fluoresce. On cotton it does not fluoresce at all.

We have with our textile fibers in this particular case the same sort of thing that we had with our mordants. That is, for Rhodamine G the silk ionizes it to an appreciable amount and the wool and the cotton practically do not ionize it at all. If this is the true explanation we ought to get something similar with mordants and we did.

We found that with zinc oxide and Rhodamine G there is no fluorescence at all; with alumina, there is a slight yellow fluorescence; and with silica there is a distinct yellow fluorescence.

We next tried violuric acid, which is not, of course, ordinarily used as a dye. The alumina lake was violet, the color of the violuric ion. Stannic oxide does not take up much violuric acid; but it does take up some and the tin lake is perfectly colorless. Here again we have the alumina as an ionizing adsorbent and tin as a non-ionizing one.

That being straightened out for the time being, we were like Lord Geoffrey Amherst and we looked around for other things to do. Dr. Crossley of the Calco Chemical Company said to us: "Can't you do something in the way of better dyeing with alizarin?" The old method had forty operations, more or less. The newer methods are better than that but nothing to brag about. Dr. Crossley said: "We make alizarin and we would sell it if the dyers could use it without trouble. Isn't there a way of doing it rather better?"

We tried two or three things. In the first place, I don't think much of the ordinary way of mordanting, and we found that one can mordant with colloidal alumina and soap without going through the preliminary stages, and that one can then dye the cloth easily with alizarin. That meant fewer operations than ever before.

That did not seem like the last word, however, and we

asked ourselves: "Why not make an alumina-alizarin lake which we will have as a pigment? Then if we peptize that, we can dye with that direct and under those conditions, at least on paper, the dyer doesn't have any more trouble with Turkey Red than he would with a basic or an acid dye on wool." (Laughter.) Actually you can do it in the laboratory. Whether you can do it in the plant or not, I don't yet know. That is quite another job,

We have been trying that same sort of thing in another way. We can dye moderately well with alumina lakes of acid dyes. Whether that is going to be of any real interest or not I don't know. Mr. Rose says no. Mr. Rose says that in this country the whole tendency is away from the use of mordants. I am not quite sure about that. He is perfectly right as far as he goes but I am not sure that the tendency isn't away from the mordants simply because the mordants mean a lot of trouble and time, and that if you could do the thing just as easily the other way you might find a change in fashion. We hope to convert Mr. Rose some day.

There is another bit of work which we have been doing which ought to interest you. If you look up the literature on the fading of dyes in light, which under ordinary conditions is practically always an oxidation—not always but it is in ninety per cent of the cases anyway—you will find that the literature is perfectly ghastly when it comes to the fading of dyes on fibers or on mordants. I will give just one or two cases to show you what you can have in that way. It is almost unbelievable.

Paranitraniline red is faster to light on cotton than on wool and you can make any hypothesis that you like to account for that. I don't care what hypothesis you make, because it can't be right. Indigo is faster to light on wool than on cotton. Methylene Blue is faster on cotton than on wool. The substantive dyes or at least the ones to which they were referring—I don't mean to say it holds for all of them—are faster on wool than on cotton, just the reverse. Quercitron—this is purely from books; I have never seen it—is said to be much faster on alumina than on tine. On the other hand, alzarin is faster on tin than on alumina. Acid Green we know is faster to light on alumina than on tin, because we did that ourselves, and Acid Green is also faster on zinc than it is on tin, so that tin is the worst of the three. But Azo Geranine is faster on tin than on zinc.

What are you going to do with a thing like that? It looks like a perfectly hopeless thing to make a theory, for because the facts go every which way. As a matter of fact, that was the time when we stopped theorizing and decided to do a couple of experiments; we got the answer which I am here to tell you.

Suppose I have the same dye on two different mordants or two different fibers and suppose that the dye is adsorbed much more strongly on one mordant or fiber (I in Fig. 2) than on the other mordant or fiber (II in Fig. 2). If we put the same amount of color on each mordant or fiber, as shown by the points B and A, we see that B is much nearer the saturation limit for II than A is for I. We postulate as one working hypothesis that, if there are no disturbing factors, the dye will be faster to light the farther it is from the saturation limit. In other words, the dyeing represented by B should fade in light more rapidly than the dyeing represented by A.

This is true experimentally, Indigo is adsorbed more strongly by wool than by cotton, other conditions being the same, and, for the same amount of dye taken up, indigo is faster to light on wool than on cotton. We determined the times necessary to practically complete fading. It would probably have been better and the differences would undoubtedly have been more marked if we had determined the times necessary to do, say, ten per cent fading; but that did not occur to us in time.

With Acid Green the order of decreasing fastness to light is alumina, zinc, and tin. The order of decreasing adsorption is alumina, zinc, and tin. With Azo Geramine the order of decreasing fastness to light is alumina, tin, and zinc. The order of decreasing adsorption is alumina, tin, and zinc. These two dyes are used in making printing lakes, which is the reason for this otherwise extraordinary selection.

With Alkali Blue the order of decreasing fastness to light is alumina, zinc, and tin. The order of decreasing adsorption is alumina, zinc, and tin; but this is not as satisfactory as it seems because the difference in adsorption between zinc oxide and stannic oxide is less than one would have liked to have it.

The results with alizarin do not fit into the picture because the alizarin is fastest to light on tin, then on alumina, and least on zinc, whereas it is adsorbed most strongly by tin. This is not so serious because we are dealing with three different colors. Alizarin is orange on tin, red on alumina, and lavender on zinc. While we do not know that this change in color is what causes the different fastness to light, we at least know that the three lakes are not comparable.

I have said nothing about the chromium, iron and copper lakes because the colored mordants introduce a complication. So far as we have gone, the dyes on colored mordants seem to be faster to light than those on colorless mordants. We have been working out the theory for the simplest case, that of colorless mordants.

The next question is whether there are not disturbing factors in some cases. Dreaper says that primuline is faster to light in mass than on the cloth. The chances are that this is experimental error and that Dreaper did not compare equal weights of primuline. On the other hand, he may be right, because I know of certain cases in which the disturbing factors are important. Lithopone, as it used to be made, was zinc sulphide adsorbed on barium sulphate. This blackened readily in the light with

formation of metallic zinc, while it is very difficult to decompose pure zinc sulphide by light. Apparently metallic zinc is adsorbed very strongly by barium sulphate, thus making the decomposition possible. In any case in which the decomposition product of the dye is adsorbed more strongly by the mordant or fiber than the dye itself is, there may be a reversal of fastness.

If the mordant acts as an oxidizing catalyst, the dyed mordant may be less fast to light than the pure dye. According to the literature this may occur with zinc oxide; but the data are not sufficiently accurate to warrant drawing a definite conclusion.

As some of you may remember, just after the war we got a particularly bad grade of hard coal. We are up in the hard coal regions. The chimneys filled up with soot. If we would take a bar of zinc, we were told, and throw it into the furnace, it would burn, of course, and the zinc oxide would go off and go up the chimney and clean out the soot. Well, it did. We don't have to do that now because the coal is rather better. I asked the New Jersey Zinc Company why that worked. They were advertising it. They said: "Evidently it acts as an abrasive (laughter) and scrapes off the soot as it goes up."

That seemed just a little "fishy." I don't believe it acts that way. But I do think that what happened was that that zinc oxide settled on the soot as it went up and at least part of it didn't come out of the chimney and probably it did act as an oxidizing catalyst, and that is one of the things we are trying to check up. We know that it acts as an oxidizing catalyst with sugar. It is said to act as an oxidizing catalyst with certain dyes and it may act as an oxidizing catalyst with this thing in this particular case.

The main conclusions that I wish to draw are as follows:

1. Under dyeing conditions the dye is adsorbed by the mordant and does not form a stoichiometrical compound with it.
2. It is possible to dye satisfactorily with a peptized lake.
3. Some mordants are good ionizing adsorbents and some are almost non-ionizing adsorbents. This accounts for the different colors of polygenetic dyes on different colorless mordants.
4. If a dye fluoresces in solution and not as a solid, it will fluoresce on an ionizing adsorbent and will not fluoresce on a non-ionizing adsorbent. If Witt had known about ionizing and non-ionizing adsorbents, he would not have developed his solid solution theory of dyeing.
5. If there are no other disturbing factors, a dye will be faster to light on the mordant or fiber which adsorbs it the most strongly.
6. If the decomposition products of a dye are adsorbed by the mordant or fiber more strongly than the dye itself, this may cause a reversal of fastness to light.
7. If a colorless mordant acts as an oxidizing catalyst, this may cause a reversal of fastness to light.
8. So far as our experiments go, dyes are faster to light on colored mordants than on colorless mordants. This is probably not always true.

DISCUSSION

Chairman Killheffer: Is there any discussion on this presentation of Professor Bancroft's?

Dr. Rose: I should like to ask Dr. Bancroft whether he examined the same dyestuff on two samples of the same mordant, one of which adsorbed better than the other?

Prof. Bancroft: Yes. If you age your mordant, of course, it doesn't take up as well, and it isn't as fast to light. We tried that. I should have mentioned it. That slipped my mind.

Dr. Rose: I might add that I have one experiment that fits in nicely with what you mention: If you take silica gel — perhaps you did that — with Fluoresceine, the fluorescence is so vivid that you see no color at all except the most brilliant yellow imaginable. It looks like the finest yellow lake possible. If you take Eosine, there is practically no fluorescence but you get a pink gelatin gel.

Prof. Bancroft: We never thought of that, and also it was getting pretty close to the time when the man had to graduate. (Laughter.) So that the only thing we tried was Rhodamine and we tried Rhodamine because that was one of the things mentioned specifically by Witt as one reason. The experiment is a lovely one on Fluoresceine. I am going to make up a sample of that as soon as I get home. (Laughter.)

Chairman Killheffer: Is there anything further in connection with this paper? If not, we will proceed to the next paper which is the one by Dr. Harris on "The Iso-Electric Point of Wool." The title of this paper has been changed, I am informed. The title is now "The Physical Chemistry of Silk and Wool."

Dr. Harris is as you perhaps know the Research Associate of our own Association. I am sure that we will listen to him with a great deal of interest. (See next page.)

WINTER MEETING, SOUTHEASTERN SECTION

The Southeastern Section of the American Association of Textile Chemists and Colorists will hold their winter meeting February 6th, Saturday, 7 P.M., at the Ralston Hotel, Columbus, Georgia.

The speakers will be as follows:

Mr. Robert Harris, Spalding Knitting Mills, Griffin, Georgia: "The Dyeing of Skein Yarns for Use in Ingrain Hosiery."

Mr. Edgar White, Technical Representative, Ciba Company, Greenville, S. C.: "The Preparation and Dyeing of Vat and Napthol Colors on Cotton Piece Goods."

Proceedings of the American Association of Textile Chemists and Colorists

The Physical Chemistry of the Proteins of Silk and Wool*

By **DR. MILTON HARRIS**

Research Associate, American Association of Textile Chemists and Colorists

A PAPER entitled "The Physical Chemistry of the Proteins of Silk and Wool" would be far too comprehensive to give in the half hour allotted but I hope to leave with you a few of the conceptions of the more fundamental properties of these proteins and what they represent with respect to some of the practical aspects in the processing during manufacture.

The application of physical chemical methods to studies of proteins has made it possible to better understand the complex character of these materials as well as give us a method of measuring any changes taking place during processing.

Silk and wool belong to the class of proteins known as the keratins. These exist in nature as very firm insoluble bodies and ordinarily speaking are immune to enzyme and bacterial attack. I say "ordinarily" since it has been shown recently that if enough surface is exposed, that is in crude suspension or in colloidal solution, these materials are attacked by enzymes.

The greatest difficulty heretofore in studying the properties of these proteins has been their extreme insolubility in ordinary solvents. That acids and alkalies will dissolve them has long been known but their action is so drastic that few of the original properties of the materials are retained in solution.

In order to study the physical properties of these materials it was necessary to put them in solution and in doing so to effect as little change as possible in the original substance.

The development of colloid chemistry during the twentieth century has been of great help to us. However, it was formerly believed that since these materials were of a colloidal nature, only laws applying to colloids could be applied to them and that the laws of true solutions did not hold. I think the research of the past ten years has changed this and that in some cases it is very necessary to apply the laws of true solutions to colloidal solutions.

As I have mentioned before, proteins are very difficult to work with. They are not volatile and only in special cases have they been crystallized. Not only that, but the molecules are so very large that it only takes an extremely small amount of acid or base to neutralize a single acidic or basic group in the protein molecule.

Although the exact molecular weights of these proteins are not known, the masses in general are known to vary greatly. A solution of protein in water may vary in character from a clear, transparent liquid, to a cloudy dispersion. In general, the masses of protein particles may vary from ten to one hundred thousand and in the case of molecular aggregates even more.

Probably the two best ways of characterizing a protein are by its solubility and its acidic and basic nature, more generally known as its amphoteric properties. I will proceed first to a short discussion of the solubility properties.

Both silk and wool are readily soluble in strong acids and alkalies but are rather stable in dilute solutions of these solvents. However, it is very probable that in effecting this solution with strong acids and bases the reaction is accompanied by hydrolysis. As early as 1913, Von Weimarn announced that concentrated aqueous salt solutions were capable of dissolving not only cellulose but such organic colloids as fibroin and chitin and that these were convertible into a ropy plastic state. This was of great interest not only from the standpoint of studying the dispersed systems of these materials but also because it offered new possibilities in the artificial fiber industry.

Since most of this work has been done on the solubility of silk I shall spend most of the time talking about that. Strangely enough, wool is not very soluble in these salts and it has handicapped many of our studies. It is very easy to obtain silk in concentrations as great as 30 to 35 per cent, in concentrated aqueous salt solutions, by heating to the boiling point for a few minutes. These salts include the chlorides, bromides, iodides, nitrates, thiocyanates and chlorates of calcium, strontium, barium and lithium. These salts have been arranged in series with respect to the anions, the dispersing power being a maximum at one end and the coagulating a maximum at the opposite end of the series. The ions arranged in order of their dispersing power are the thiocyanates, iodides, bromides and chlorides. In other words, if you were in

*Paper presented at Annual Meeting, Boston.

a manufacturing plant you wouldn't be very apt to use thiocyanate in the processing of silk.

I think people with experience in boil-off of silk know that small amounts of sodium carbonate are used to buffer the solution and keep up the pH but if you get much over a tenth of a per cent of carbonate in the solution you get distinct tendering of the silk, and if you carry that to a maximum, that is, use a concentrated carbonated solution, you can actually dissolve your silk. It is evident that the dissolving of silk is preceded by a decided tendering. In general these salts are very much less powerful solvents than the strong acids or alkalies being as much as two hundred to five hundred times less powerful.

Concerning theories on the solubility, there are two:

First, introducing a charge in the protein molecule which tends to extend the surface or scatter the molecules;

Second, increasing the association of protein molecules with water molecules, which will tend to lessen the interfacial tension.

Von Weimarn's theory is that in the dissolving of silk the predominant feature is the hydrative capacity of the salt and not the chemical nature of the substance. Hardy postulates another theory. He assumes that the salt adds on to the amino group, changing the nitrogen from trivalent to pentavalent.

In our work, solutions of the silk were prepared by dissolving the fibroin in either a fifty per cent lithium bromide or a seventy per cent calcium thiocyanate solution, by heating to eighty degrees Centigrade for a few minutes. These solutions are generally diluted and a few drops of toluene added to prevent any bacterial decomposition. Then they are dialyzed until the water surrounding the dialyzing bags gives no test for the salts present. By this method you can obtain solutions of silk up to about five per cent. But these solutions are rather concentrated and tend to precipitate rather rapidly. Therefore if you use a one per cent solution, or less, you have a very stable and uniform solution.

With the obtaining of satisfactory solutions it is very easy to obtain many of the properties of Silk. Fig. I shows the decomposition of the silk which was followed chemically by the measuring of the amino-nitrogen, using the Van Slyke apparatus.

I used three normal hydrochloric acid because one normal hydrochloric acid gave a solution so close to the isoelectric point that the silk tended to precipitate. Even in this concentration it becomes evident silk is much more stable to acid than to alkali. Heating in a water solution of the same intensity gave no appreciable decomposition of the silk, showing the silk to be rather inactive in ordinary water solutions.

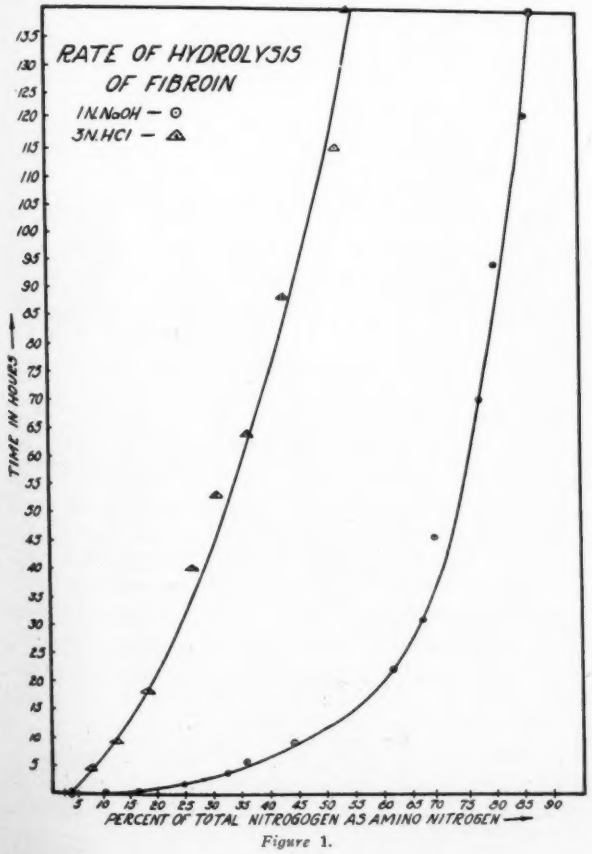

Figure 1.

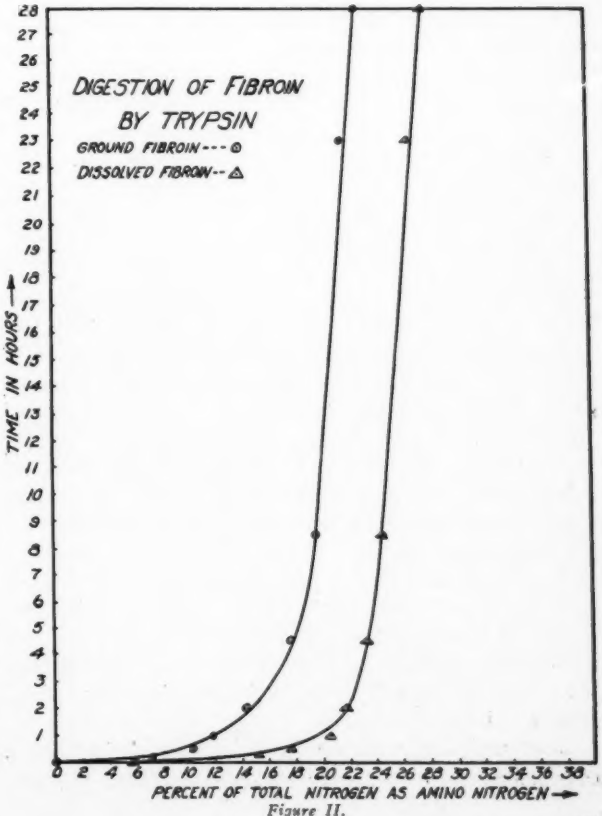

Figure II.

Fig. II shows the digestion of fibroin by trypsin in two types of silk solutions, one prepared chemically by dissolving the silk in our salt solutions, the other by grinding the silk to a very fine powder and suspending it in the desired medium.

There is a strange phenomenon here. There is approximately five per cent more amino-nitrogen in silk solutions prepared chemically. Apparently when you dissolve this silk you break down several of the peptide linkages in the peptide structure. The remarkable thing about this is that regardless of how long you heat your silk in these salts you always get a constant amount, approximately five per cent, of the amino-nitrogen. The only difference in these two curves is that the additional five per cent of the amino-nitrogen in the chemically prepared solution persists all the way through, showing that the rate of digestion, whether the silk was prepared by chemical or mechanical means, was independent of the method of preparation and that the actual digestion depended on the surface exposed.

There are several other slides on the properties of these silk solutions but as long as they were used in determining the iso-electric point of silk, I will show those later in the discussion of the amphoteric properties of the protein to which I will now proceed.

An acid may be defined as a substance which in solution gives, by disassociation, positive hydrogen ions or takes up negative hydroxyl ions. Similarly a base is defined as a substance which gives off negative hydroxyl ions or takes on positive hydrogen ions. An amphoteric substance is one that combines both of these properties; in other words, it is capable of ionizing either as an acid or a base. Since the protein molecule has both acidic and basic properties, it follows that it is negatively charged in alkaline solutions and positively charged in acid. Wool and silk are both acid proteins. In other words, the acid group predominates in the molecule.

The iso-electric point is generally defined as equal to the reaction of neutrality. In other words, you have two characteristics at that point; the concentration of the negative ions, of the amphoteric substance, equal to the concentration of the positive atoms and the sum of concentrations of both, is a minimum at that point.

What does that mean? If we have an acid iso-electric point we add enough acid to this solution to repress the ionization of the acid group until it is equal to that of the basic group.

When one says that the iso-electric point is three or four he does not mean that the iso-electric point is three or four but means that pH 3 or 4 is the hydrogen ion concentration of the solution necessary to suppress the ionization of the acid group so that you have equal ionization in both directions.

In a solution of a protein therefore you may have electrically neutral protein particles and electrically charged protein ions, and the properties of these solutions will depend on the relative proportion of both of these. At the iso-electric point we have the neutral particles. It becomes at once obvious then that the iso-electric point is a point of maximum or minimum properties and actual experimental work has shown that the solubility, viscosity, migration in the electric field are all at a minimum at the iso-electric point.

A number of these properties have been used as methods for determining the iso-electric point.

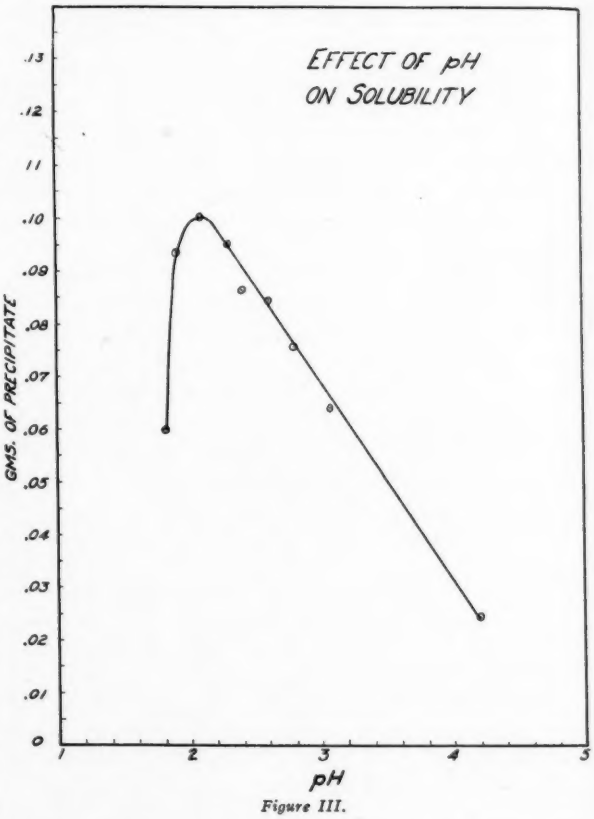

Figure III.

Fig. III shows the effect of pH on solubility. The precipitates have been determined quantitatively at various pH's. This gives a definite maximum precipitation or minimum solubility at a pH of approximately 2.2 which may be taken as the iso-electric point of silk.

Fig. IV shows the relationship of pH to viscosity.

I may mention at this point that these curves are rather easy to obtain. The solutions are very stable and very uniform, giving very smooth curves. I am very sorry to say I have never been able to duplicate this work with wool. I have not been able to obtain any satisfactory solution prepared by chemical means with wool.

Probably one of the best ways to study the amphoteric nature of a protein, and one which may be used as a method of determining its iso-electric point is by measur-

ing the migration in an electric field. This migration of particles in suspension or in solution is known as cataphoresis or electrophoresis. Cataphoresis or electrophoresis methods have been used in biological work for studying blood cells, and bacteria; they have also been used in the study of cellulose, clay particles and oil emulsions.

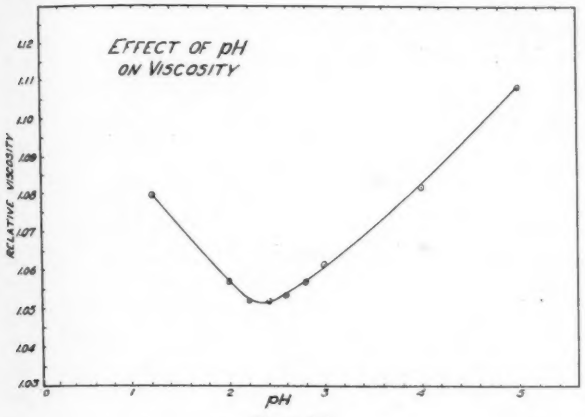

Figure IV.

I think it is important enough and there is enough application of cataphoresis measurements for the studying of the properties of silk and wool that I should give you a very brief explanation of what a cataphoresis apparatus is and a short discussion on the theory of cataphoresis.

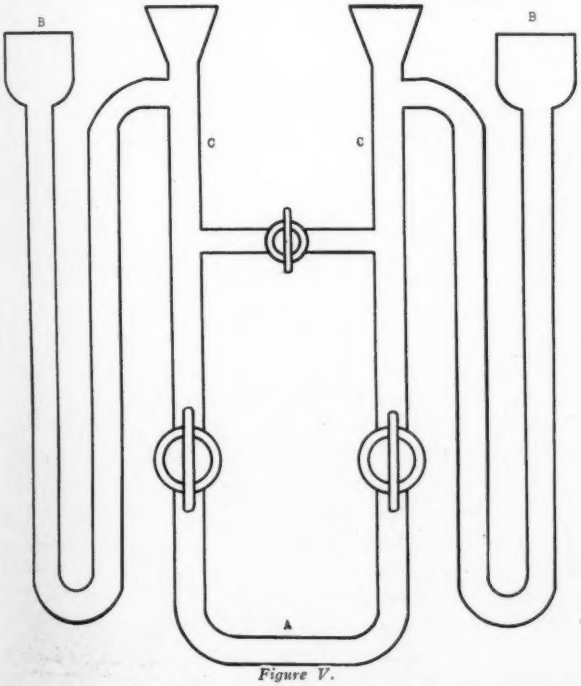

Figure V.

Fig. V. This is the old type of cataphoresis apparatus which is sometimes still used, known as a microscopic cataphoresis "U" tube. The diameter of the tube is fairly large. The solution to be studied is placed in A at a definite pH. A similar buffer solution without the protein is placed in the rest of the apparatus and direct current applied at BB. After it is allowed to run for a certain length of time the solution in CC is drawn off and analyzed. Depending upon the charge of the particles, the protein has either gone to the positive or negative pole. The trouble with this apparatus is it gives you a broad iso-electric range. It is hard to get a very definite minimum. It is so large that diffusion, convection currents and gravity play a large part.

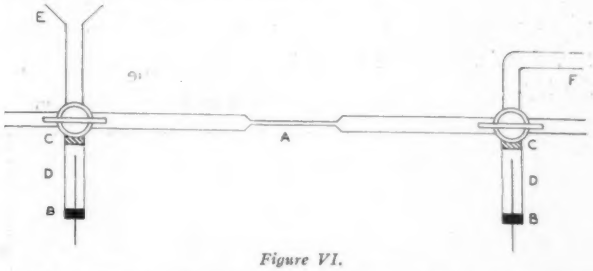

Figure VI.

Fig. VI is the new type of apparatus used. It has been used considerably by Dr. Abramson in Harvard University.

The cell A is very small. It is three and a half centimeters long, one centimeter wide, and only a half millimeter in thickness. The diameters of the connecting tubes are rather large. DD are non-polarizable electrodes composed of copper, copper sulphate, while the porous plugs, C, are made of Plaster of Paris saturated with KCl. They are put in there to prevent diffusion.

The solution to be studied is put in at a definite point in E and allowed to run out of F until the cell is completely filled and there are no air bubbles. Then A is opened to the electrodes.

The whole apparatus can be placed on the platform of a microscope, a direct current of 220 volts applied, at each electrode, and by focusing the microscope at the proper depth you can measure the velocity of the particles across the field. The microscope eyepiece contains a five or ten millimeter graduation and a stopwatch is used as the timing device.

Just a brief explanation of the theory of cataphoresis. When the movement of successive layers of suspended particles in an electro-negative suspension is measured in a closed system such as has just been described the liquid moves to the cathode. It would seem as though the particles were positively charged. As you go down toward the center of the tube you come to a place where you get no movement of the particles and then as you proceed to the center of the tube the velocity increases in the opposite direction. The movement of particles with respect to liquids is known as cataphoresis and the move-

ment of the liquid along the wall with respect to the stationary surface is known as electro-osmosis.

Since there is a movement of the liquid with respect to the wall it is apparent that the water must be oppositely charged to the glass surface. In other words, at the interface of liquid and wall there is apparently a double electric layer existing. This is sometimes known as the Helmoltz double layer theory. Apparently the glass surface is negatively and the water positively charged.

There is a mathematical derivation to determine where the proper depth to measure your velocity of particles is in a given cell. I won't go into that now but suffice it to say for this type of cell the true velocity of the particles is obtained at four-fifths the depth of the cell from the top, that is, one-fifth from the bottom or one-fifth from the top.

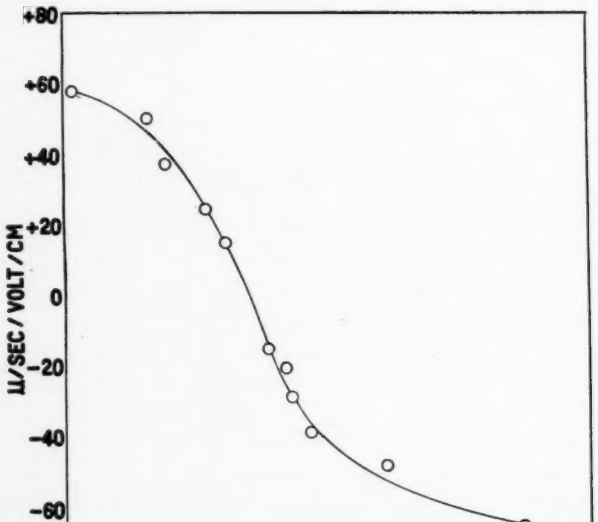

Figure VII.

Fig. VII shows a typical pH—mobility curve. I do not want this to be taken as the final iso-electric point of wool but it is pretty close. This particular curve gives an iso-electric point of wool of about 3.3-3.4.

There is something remarkable there in that we get a curve very similar to titration curve for a weak acid or a weak base. When you consider that we are working with extremely large particles compared with true molecules and that we get a disassociation curve which is very similar to the disassociation of a weak acid or a weak base, it is very evident that some disassociation takes place. I do think there is some absorption taking place but the curve is largely affected by the ionization of the acid or basic groups.

I have a few practical applications of this. I have a few samples of dyed materials. I know nothing of practical dyeing but I attempted, by the shape of the curve of different types of wool, to predict how the dyeings would go on a few simple dyes.

On the acid side of the iso-electric point the particles will move to the negative pole. In other words, they are positively charged. At our iso-electric point we have a neutral protein and therefore we get no movement of our particles. On the alkaline side they move to the positive pole and therefore are negatively charged.

Fig. VII is a curve for pure raw wool which has been cleaned by use of organic solvents and all chemical reactions, at least that we know, have been excluded.

If we take carbonized wool we get a very different curve. In the region pH 2.5 to 5, the carbonized particles appear to be much more positively charged. That is a very strange phenomenon. If the potential of carbonized wool is much more positive you would assume that an acid dyestuff being negative in nature would be more readily absorbed on carbonized wool than it would be on uncarbonized wool, and that is what we found to be the case.

This wool was dyed with Alizarine Saphirole B. The pH of both solutions was kept identical. Al the excess acid was washed out of the wool, and the physical conditions were kept the same.

Similarly, we reason that basic dyes should be less strongly absorbed on the carbonized wool because that is more positive. Actually, that is what happened. This is a piece of uncarbonized wool dyed with Methylene Blue 2B. This is the same of carbonized wool. If anybody wants to see these afterwards, I will be glad to show them.

In the case of silk which has a much lower iso-electric point, in other words, is far more acidic, we get a curve similar to that in Fig. VII but shifted to the left. In other words, at any given point silk is more negative than wool. From that you would expect that, silk being more negative than wool, it would absorb more basic dye. Actually, it does. I know nothing as I say of the practical side of dyeing, but I am offering this as purely theoretical speculation.

One other practical use of the iso-electric point studies: There are probably a good many silk people here who have had quite a bit of experience in the boil-off of silk. Sericin of silk is boiled off generally in a soap solution at about pH 10. The iso-electric point of sericin is about 3.6 to 3.8. At the iso-electric point a protein is very insoluble and the farther you go away from the iso-electric point the more soluble it becomes. Silk is a very insoluble thing and you may get far away from its iso-electric point and still find it comparatively insoluble but it will be far more soluble than at its iso-electric point.

I have had several people ask me if you could boil off silk in an acid solution, the idea being that alkalies do

(Continued on page (76) 96)

Proceedings of the American Association of Textile Chemists and Colorists

A Study of the Stress-Strain Curve on Rayon*

Part I. The Method and General Conclusions

By DR. HENRY GREEN
Hathorne and Green

WHAT happens to a rayon fiber when it is stressed? Does it first stretch elastically and then flow plastically? Or do both types of elongations (elastic and plastic) take place at the same time?

It seemed possible that questions of this type could be answered by a careful study of the lower end of the stress-strain curve. It would be necessary, however, to determine the percentage elongations with considerably greater accuracy than the standard routine testing machines are able to do.

In addition to the above questions, it can readily be seen that investigation of the stress-strain curve should reveal methods for determining certain constants of the fiber that are at present disregarded by the rayon manufacturer. Such constants, for instance, as true elastic limit, modulus of elasticity, elastic recovery and the plastic properties such as yield value and mobility. Comparisons of these factors could very well be of interest in comparing those of rayon with those of real silk and other natural fibers. In this manner a new basis for research investigation could be established, bringing out the inherent differences between synthetic and natural fibers, and so indicating the directions in which changes must be made in order to simulate the properties of the natural fibers.

The micelle structure of rayon is evidently of such a nature that both elastic and plastic elongations are possible. This condition can be visualized by the diagrams in Figure 1.

The elastic limit is given by that tension beyond which *complete* elastic recovery is no longer obtainable.

Hook's law states that below the elastic limit, stress is proportional to strain. The element of *time* is not included in this law, it being assumed that equilibrium is obtained practically immediately. The law of plastic flow is not at present known with any degree of accuracy, but if we assume that all telescopic layers in a plastic medium commence flowing simultaneously, then from purely mathematical considerations a linear relationship ensues, the curve cutting the pressure axis as shown in Figure 2.

The point to be emphasized here is that *time* enters the viscous and plastic laws of flow while it is not taken into consideration in Hook's law.

The method described in this paper for determining stress-strain curves is intended neither for a routine test nor as a substitute for any of the standard tensile machines now on the market. It is simply a method of research, and in this capacity is hoped that it will be of some interest and value.

When a constant tension is applied to a thread, elongation takes place. If the tension is not too great, the rate of elongation decreases to zero after an elapse of time. At this point equilibrium is established between the external applied tension and the internal stresses resulting from the strained condition of the thread. When this tension is plotted against its corresponding percentage elongation, a stress-strain curve is produced where the element of time has been entirely eliminated. It is obvious that this type of curve must differ from that made with a continuously *increasing* tension. In this latter case any definite tension, say 25 grams, exists only for an infinitely small length of time. Just how far the thread would ultimately stretch under a 25-gram tension can be determined only when this particular tension is allowed to act over a considerable time. However, it must be borne in mind that by the time the 25-gram tension has been reached the thread has been subjected to an infinite number of tensions ranging from zero to 25 grams.

If it be assumed that an elongation of one one-hundredth of an inch can be estimated or measured and if a weight be attached to a thread one hundred inches long in a vertical position producing such an elongation, then an accuracy of one one-hundredth of a per cent is obtainable. On the other hand, if the thread is put in a horizontal position supported at both ends by two pegs (the weight being placed in the middle) and we still assume

*Paper presented at Annual Meeting, Boston.

that one one-hundredth of an inch can be estimated, then the accuracy with which the percentage elongation can be determined will be from fifty to one hundred times greater than previously. The reason is obvious, for the total distance descended by the weight represents only a small fraction of the elongation to which the thread is subjected. This latter scheme is the one carried out here, thus making it possible to study the stress-strain curve very close to the origin.

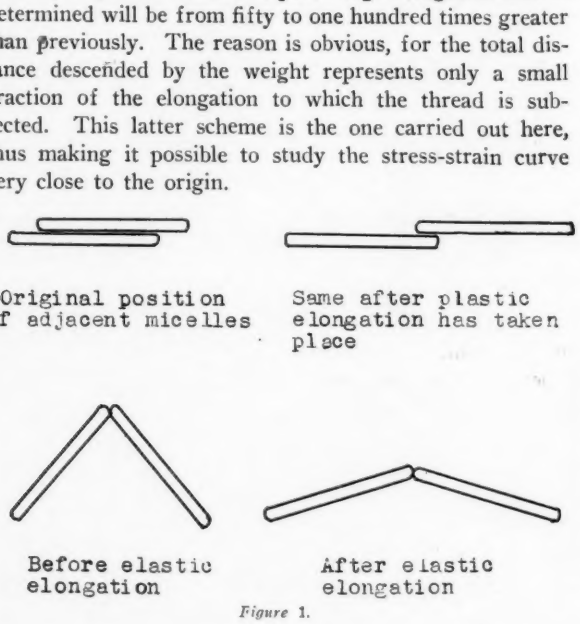
Original position of adjacent micelles
Same after plastic elongation has taken place
Before elastic elongation
After elastic elongation

Figure 1.

The method requires no special apparatus, simply a set of weights ranging from one-half gram to one hundred and fifty grams to which small hooks are attached. The thread is suspended horizontally between two pins exactly one hundred inches apart and about five feet above the floor. Half way between these two pins a vertical scale is fixed divided in tenths of an inch. If ten points on the stress-strain curve are desired, ten lengths of thread are suspended between the two pins. The series of weights is then placed on the threads and after a lapse of time the distance to which each weight has descended is measured; these are the only measurements taken, all subsequent calculations being made from them.

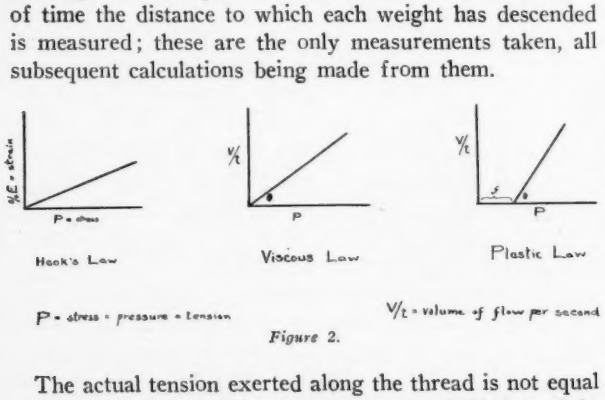

Figure 2.

The actual tension exerted along the thread is not equal to the weight suspended but is equal to one-half the weight divided by the cosine of alpha. See Figure 3.

The percentage elongation is determined by simple calculation from the right angle triangle abc, viz:—

$$\%E = \frac{b-a}{a} \times 100$$

Therefore,

$$\%E = \left[\sqrt{1 \div \frac{c_2}{a_2} - 1}\right] \times 100$$

From the parallelogram law it can easily be shown that tension, P, is:—

$$P = \frac{\frac{W}{2}}{\cos \alpha}$$

If the thread is pulled sufficiently tight between the two pins so that no sag exists, a certain indeterminable tension is introduced. Theoretically, as long as the thread has any weight at all this tension is infinitely great, that is, if the thread actually assumes a perfectly straight horizontal position. In practice, however, the weight of the thread being very small and a close approximation to a straight line being all that is necessary, the tension introduced is not so serious. This tension can be eliminated entirely by allowing the thread to sag at the start and correcting later for this condition.

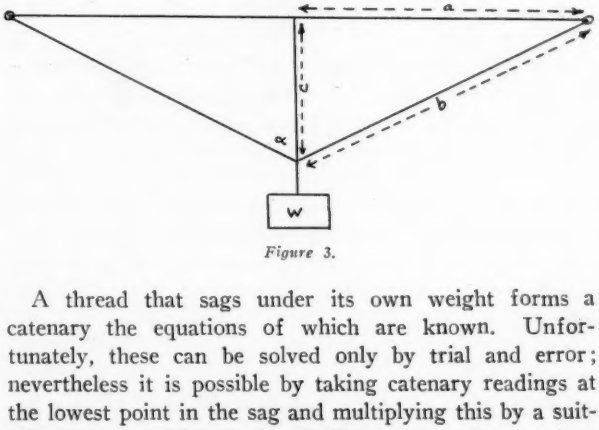

Figure 3.

A thread that sags under its own weight forms a catenary the equations of which are known. Unfortunately, these can be solved only by trial and error; nevertheless it is possible by taking catenary readings at the lowest point in the sag and multiplying this by a suitable factor (which is practically constant for a given set-up) to obtain a figure equal to that where the thread would be if pulled down tight without stretch. From this reading the increased length from the standard length of one hundred inches is attained; the correction is then made in the following manner:—

$$\%E = \%E_2 - \%E_1$$

where $\%E_2$ is the percentage elongation obtained with the weight attached, and $\%E_1$ is the percentage elongation derived from the sag reading. This equation holds very closely when the thread is originally as long as one hundred inches.

The weight of the thread itself produces an added tension which can be corrected for by adding to the tension an amount equal to half the weight of the thread divided by the cosine of alpha. This additional tension is not

uniformly distributed throughout the thread but is equal to zero at the point of application of the weight and to its full value at the pin.

It will be found convenient, if many calculations are to be made, to plot percentage elongation against c and also to plot the cosine of alpha against c. Percentage elongation and cosine of alpha are then determined directly by interpolation.

As we are dealing here with very small percentage elongations it becomes necessary to guard against temperature and humidity changes. As these factors produce effects equal in some cases to the elongation measured, it is necessary that the thread be conditioned over a period of twenty-four hours and that the experiments be carried out in a room in which the humidity and temperature are controlled. Even though such control is not available a great deal of information of interest can be obtained. It is only when full advantage of the accuracy of the method is desired that temperature and humidity must be taken into consideration.

The method of carrying out the complete experiment is as follows:— eight or ten threads are fastened between the pegs and allowed to sag an inch or two at the center. Readings are then taken giving catenary values for c which are multiplied by the factor 1.155. The percentage difference in length (from the original length of one hundred inches) can then be calculated from the chart which plots c against %E. This gives the value of E_1. Different weights are now hung on the threads and allowed to stay there until equilibrium has been obtained. This will require from two to three weeks as a rule. Readings are now taken of the various distances the weights have dropped. From these readings tension and percentage elongation are calculated. When these factors are plotted, the stress-strain curve is produced. The weights are now removed and the threads allowed to contract for a period of approximately two to three weeks. Catenary readings of c are now taken, multiplied by the factor 1.155, and percentage elongations again calculated. These last percentage elongations are plotted against the final tension to which the threads were subjected before the weights were removed. We now have two curves such as are shown in Figure 4.

It will be noticed that these curves are free from the usual steps prevailing in the customary stress-strain curves. If any part of the curve is linear it is that portion close to the origin, and in the case of rayon this does not extend much beyond one-half per cent elongation. If the material is truly elastic under these small tensions, it must give a linear relationship according to Hook's law. One radical departure from Hook's law, however, occurs at this point and that is that considerable time must elapse before elongation stops. This condition could arise if we had an elastic structure imbedded in a viscous or plastic medium, thus retarding the stretch and introducing the

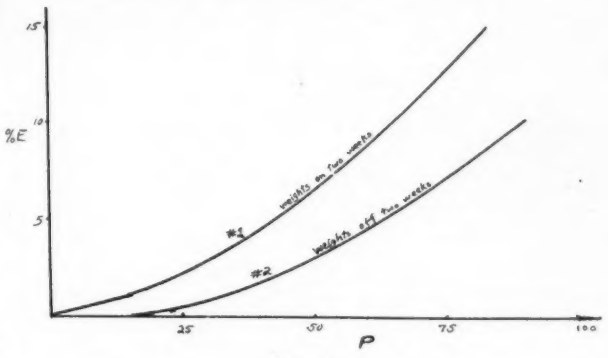

Figure 4.

time element. It is not to be assumed that such an independent medium actually exists in rayon but that the micelles themselves are so arranged that they constitute both a plastic medium and a stretchable elastic structure.

It is apparent that any departure from linearity constitutes a type of elongation differing from purely elastic stretch. The surprising thing discovered so far is that this condition of non-linearity exists so close to the origin, which means, of course, that plastic flow commences almost as soon as the thread begins to elongate. Even in the case of real silk this condition exists although the curve seems to be linear perhaps to the extent of two to three per cent elongation. The true elastic limit is apparently that point where plastic flow commences. This does not mean that elastic elongation ceases there, for as a matter of fact, it continues stretching elastically while at the same time it is undergoing plastic flow. In Figure 4, the bottom curve is the plastic flow curve of rayon and is indeed similar to such curves obtained from paint and other slightly plastic suspensions. The tangent of this curve is a function of the mobility, that is, it indicates the ease with which the material flows after the yield value has been passed. The intercept of this curve on the tension axis is a function of the yield value. The vertical distance between the two curves at any particular point gives the amount of elastic stretch, while the distance between the tension axis and the lower curve gives the corresponding amount of plastic elongation. The modulus of elasticity can be obtained only from the extreme lower end of curve No. 1 and is equal to the cotangent of the angle between the curve and the tension axis. In determining the modulus of elasticity the tension should be divided by the area of cross section of the thread, giving results in grams per square centimeter.

The question arises as to why plastic flow stops after the yield value has been exceeded as shown in curve No. 1, Figure 4. The most obvious explanation is the fact that in rayon fibers the yield value is not a constant as in the case of paints and other plastics of similar nature but increases as the micelles align themselves during the process of elongation. As alignment increases more micelles

come in lateral contact with each other thus increasing the frictional resistance to flow. In this manner the yield value is built up until it reaches a point where flow stops. Naturally such a building up cannot be increased indefinitely and eventually the tension will reach a point that will exceed the maximum possible yield value of the fiber. When this point is attained the material will continue to flow until rupture occurs.

In a subsequent paper experimental data will be given showing curves and factors for various types of rayon in comparison with real silk. While these differences are known in a general way it is a decided advantage to the research investigator to have been expressed in the form of curves and comparable figures.

Discussion

Mr. Quig: Dr. Green calls our attention to the fact that the elasticity of rayon is very low, and he could have gone on and talked longer and told us some of the relations of low elasticity in rayon to the kind of rayon fabric which is being produced today.

He called attention to the fact that the elasticity of rayon is much lower than that of silk.

We know that there is a lot of non-uniform dyeing fabric being produced.

In an article in the American Dyestuff Reporter recently Mr. Hathorne called attention to the fact that stretching of rayon in the manufacturing process, in warpping, slashing and weaving, gave non-uniform dyeing in the finished fabric unless the rayon was not stretched beyond its elastic limit and unless it were allowed to contract during the finishing operations.

The rayon manufacturer, from what Dr. Green has said, has a definite part and a definite problem, namely, to increase the elasticity of rayon, but I think a great deal of good could be done by the members of this Association realizing the properties of this synthetic fiber and then trying to spread the gospel of handling rayon the way it should be handled.

If we did so we would get better results than we are getting today.

Uneven tensions in any part of the operation—winding, warping, slashing, or weaving—contribute to the nonuniformity that we are getting.

The wet strength of rayon is about one-half of the dry strength. In view of what Dr. Green has said about elongation and elasticity you see that we are working with a much more dangerous state when rayon is in the wet state.

There don't seem to be any set rules regarding humidity conditions, the humidity at which we should process rayon. People disagree about that. Some mills are spending a lot of money to control their humidity during the daytime and put all of their warps on their warp mills and then through the night they discontinue it. That can't do anything but produce non-uniformity. And while I realize there is great expense connected with humidification, in some cases it probably would be better not to humidify at all and to hold to a certain humidity during the daytime, than discontinue it at night.

One way to handle the situation, of course, would be to take the warps off the warp mills.

People say, "How much should we stretch during the sizing operation?" "During the slashing operation, etc.?"

They are stretching rayon anywhere from two and three per cent up to fifteen per cent. Elasticity is low. It is easy to go beyond the elastic limit.

Enough is not known about that and somebody has to find out about it—just what we are doing.

I have talked to some members of this Association and some of them have felt that it wasn't the business of this Association. I say it is. We are all interested in securing as uniform a dyeing fabric as possible.

The attitude of the finishers and dyers might be that that finisher or dyer is a good finisher or dyer if he can take something which is non-uniform inherently when it is delivered to him and deliver it to the man who is buying the cloth in a better condition. I do not think that should be the attitude of a technical association like this.

Chairman Killheffer: Has anybody else anything to say?

Mr. C. H. Clark: May I ask if it is possible to test rayon after it has gone beyond its elastic limit and then identify it as such in comparison with a fiber that has not been so stretched?

Chairman Killheffer: Dr. Green, do you want to answer that?

Dr. Green: You mean to find out whether it has already passed its elastic limit?

Mr. Clark: That is, in examination of the grey cloth.

Dr. Green: I couldn't give any general rules for that. Each rayon manufacturer might know his own product and be able to tell. As I have found out, elastic limit is very low and any stretch over one per cent has already passed what I would call its true elastic limit. Plastic flow has also entered in at that period and you don't completely recover that when the tension is released. So if there is any stretch at all of any great amount you can almost assume that the elastic limit has been passed to a certain extent.

Professor Schwarz: I haven't experimented with rayon (which I hope to do later) but I have been able to identify in at least two cases silk which had been pre-stretched. That can be done under polarized light as we illustrated on the screen a little while ago.

Dr. Appel: Mr. Chairman, this matter of the rayon stress-strain curves is certainly one of the most important problems for study. There is the related problem of the tensions and times—the time and tension problem in the processing of the material.

You pointed out that time is a very important factor. We ought to know a lot more about the tension applied to the yarns in the processing and the time of the application of the tension because the amount of plastic flow depends on the time at which the load is applied.

Chairman Killheffer: Is there anything further?

Before we have the next paper I have been asked to call your attention, while you are all here together, to the fact that the next annual meeting will be in the South, very likely with the Piedmont Section in Charlotte and we would like you to bear that in mind.

Next on our program is a paper entitled "Suggestions for Standardizing Sulphonated Oil Analysis," by Professor Grimshaw. (Applause.)

. . . Prof. A. H. Grimshaw presented his prepared paper . . . (Applause.)

Suggestions for Standardizing Sulphonated Oil Analysis*

By **PROF. ALBERT H. GRIMSHAW**
North Carolina State College

THE reason for selecting the subject mentioned in the title of this paper may be traced to a paper read by the author at a meeting of the A.A.T.C.C. in the Piedmont Section in January, 1928. The subject of that paper was "Methods of Testing Sulphonated Castor Oils for the Determination of Their Fatty Content."[1]

At the meeting where this paper was read, there was considerable discussion as to which of the methods outlined were the best. The paper was published in the AMERICAN DYESTUFF REPORTER and the article was also discussed in later issues by well known authorities on sulphonated oil.[2]

Dr. Stadlinger[3] in the March, 1931, issue of *Melliand* and Ralph Hart[4] in the AMERICAN DYESTUFF REPORTER of April 27, 1931, also mention this article in conjunction with articles of their own on standard testing methods.

Referring to Mr. Hart's article, there is an editor's note which agrees well with the present paper. It reads as follows: "In view of the desirability of an agreement among Textile Chemists upon a standard method for analyzing sulphonated oils this article by Ralph Hart, who originally proposed the standard methods now used by the American Leather Chemists Association, should be of interest to all textile chemists."

Dr. Stadlinger[3] said in part: "Turkey red oil and the textile oils similar to turkey red oil have gained tremendous importance in the textile and leather industries. However, no field in the chemistry of fats shows a greater confusion of what is what than this one. This fact was referred to by A. H. Grimshaw three years ago in his paper 'Methods of Determination of the Fatty Contents of Sulphonated Castor Oils.' There is always confusion about the meaning of [percentage]. The testing methods are a very sore point. A questionnaire which was sent out has shown that there exist about twenty-five different testing methods to determine the actual fatty matter. Needless to say the results obtained from these methods usually differ."

Dr. Stadlinger also states that the efforts of the German chemists through the cooperation of the "Verband Deutscher Tuerkisch-Rotoel-Fabrikanten, Krefeld" and of the "Wizoff" to create standard methods have been successful. He expects the textile chemists and the leather industries to accept these methods in Germany.

Here in the United States, the American Leather Chemists Association have already shown us the way and we should get our producers, consumers and chemists together to form methods which can be used for analysis in everyone of our laboratories so that every analysis would be performed by standardized methods.

A number of years ago, the author was talking with Mr. Appel of the Bureau of Standards about this very subject, and this past summer this Bureau has been doing some good work along this line. Mr. Gilbert has had charge of the work and in a letter which I had recently from Mr. Gulick of National Oil Products Company, he writes as follows: "I thought that you might be interested in hearing that there is a movement on foot at the present time for the organization of a Sulphonated Oil Manufacturers Association. One of the first things which this association intends to do is to cooperate with various agencies in the promulgation of standard practice, nomenclature and analysis, with respect to sulphonated oils. There is a joint meeting between a committee of the pro-

*Paper presented at Annual Meeting, Boston.

posed association and the U. S. Bureau of Standards in New York November 24th to discuss this matter."

Several who attended this meeting have written to the author telling of this meeting which shows how much the manufacturers are interested as well as the United States Government.

Mr. Hart also mentions the request of the Bureau of Standards in his article "Commercial Grading of Sulphonated Oils" which was printed in the AMERICAN DYESTUFF REPORTER of August 31, 1931.

From the above we have covered somewhat the interest of others besides the A.A.T.C.C. and have also called attention to the theoretical reasons for wanting *Standardized Methods.* Let us now review a few of the present methods as directed by various authorities. First we will discuss *Moisture.*

Dr. C. I. Post[5] writes in a pamphlet reprinted from *Oil and Fat Industries* of August, 1929: "*Moisture*—In an analysis of sulphonated oils the moisture content is of extreme importance since oils are bought and sold largely on this factor alone." He writes considerably more of much interest and recommends the method of using dry oleic acid carefully weighed and then adding the sample and again weighing accurately, then dry at 100 to 102 degrees Centigrade to constant weight.

In the A.L.C.A. method, we find that the sample is distilled with or in xylol. W. H. Thomas[6] recommends the xylol method with these additions, "If foaming interferes, red oil (oleic acid) or tartaric acid may be added. Glass beads may be added to control bumping." Besides these methods, you all have heard or used some that varied from them to some degree.

FATTY MATTER

As already mentioned, Stadlinger told of about twenty-five different methods, and in an article written by the author, results were given of about fifteen different methods on three different oils. These tests covered Volumetric, Gravimetric and Extraction methods; no two of the numerous tests gave identical results.

As with the two constituents mentioned, the author has found that now two laboratories of his acquaintance are using the same methods for analysis with possibly analysis of ash being an exception. Instead of analysis of ash, we should say determination of percentage of ash. In a complete or semi-complete analysis where analyses are made for the percentage of such constituents as SO_3; inorganic matter, moisture, total fat, unsaponifiable matter, etc., it would not be right that a manufacturer possibly having analyzed his product by one method should have his product analyzed by another method which might possibly show his product to a disadvantage. Something should be done about such a condition.

The work done by the A.L.C.A., the German chemists, and now being planned by the Bureau of Standards and the Association of Sulphonated Oil Manufacturers should spur us on to make good in our own Association by planning for standard methods in cooperation with them.

This is where we wish to make suggestions. In no way do we wish to say that certain methods should be made official. If asked what we think are good methods, we would refer the members to the *Textile World*[7] of March 14, 1931, where some methods are described. Some of you undoubtedly would find points about these methods with which you did not agree and so you could offer some improvement. That is exactly what you should do, either present your own methods, or give helpful criticism on methods which may be presented.

SUGGESTIONS

First. We would suggest that the President of A.A.T.C.C. appoint a sub-committee of the General Research Committee to look into the feasibility of doing at least as much along this line for the textile industry as the A.L.C.A has done for the leather industry. We suggest that this committee be composed of members of the A.A.T.C.C. representing at least three manufacturers, three salesmen and three mill chemists and have Professor Olney as Chairman, ex-officio. In order that this committee be of the utmost value, each member should have a knowledge of analytical chemistry.

Second. As the AMERICAN DYESTUFF REPORTER is our official organ, it is suggested that the chairman shall have a notice conspicuously placed in several issues of the REPORTER somewhat on the following lines: "Will ANYONE interested in having STANDARD METHODS OF ANALYZING SULPHONATED OILS please send in methods and remarks to the chairman." If members did not show enough interest to send in their favorite analyses they certainly could not have any complaint to make if their favorite analyses were not adopted.

Third. As replies came in, they should be printed in the AMERICAN DYESTUFF REPORTER along with a request that criticisms be made and sent to the Chairman. These criticisms would all be examined by the members of the committee and all thought worthy would then be printed. The chairman would not have much to do until the criticisms came in as the members of the committee could read the analyses as they appeared in the REPORTER and then could study them and send in their own criticisms and those of other chemists with whom they came in contact.

Fourth. If the analyses and criticisms are printed as fast as they come in to the chairman, then the committee should have enough data on hand by October, 1932, so that they could form a proposed set of methods which they can present as their recommendation at the Annual Meeting in December, 1932.

Fifth. These recommendations should be printed in the REPORTER at least two issues before the Annual Meeting in order to give our members the chance to study them.

Sixth. The committee should decide whether or not,

other sulphonated products such as mineral oil, tallow, etc., should be included with the castor oil, olive oil, or glycerides of the sulphonated groups as generally used in textiles.

Seventh. As it is possible that each section may not have representation on the committee (due to the size of the committee), it might be well to ask the Chairman of each section to speak a few words at each of the quarterly meetings in regard to this subject. Possibly, he could act in an ex-officio capacity in helping to secure data to send to the REPORTER.

Eighth. It is suggested that the A.A.T.C.C. cooperate in every way with the Bureau of Standards and the proposed Association of Sulphonated Oil Manufacturers.

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DISCUSSION

Chairman Killheffer: There seems to be as much need for a uniform method of analysis in oils as there is in liquor. (Laughter.) Perhaps the same committee might handle both. I don't know whether Professor Olney would do as the chairman, or not. (Laughter.)

Professor Olney: Mr. Chairman, those who were present this morning may remember that we were talking of organizing a new sub-committee on general analytical methods as applicable to the textile industry. It may be, in the light of what Professor Grimshaw has said, that in addition to that we should have a special committee on the matter of sulphonated oils.

I had some talk with Professor Grimshaw this noon. I have already asked him to serve on such a general subcommittee on analytical methods and I would like to ask him, in the light of what he has said and his study of the subject, whether he believes that that could be handled as a part of such a sub-committee or whether there should be a separate sub-committee on that one subject.

Professor Grimshaw: Professor Olney, I have talked with some of the oil manufacturers, salesmen, and users of sulphonated oil and I rather think that they disagree so much among themselves that we had better have a separate committee. (Laughter.)

Professor Olney: I think that we can proceed to the appointment of such a committee. I right now will ask you to serve on that committee.

Professor Grimshaw: I didn't put my name on that one. (Laughter.)

Chairman Killheffer: Besides the chemists on that committee and others particularly disinterested, Professor Grimshaw, how many referees do you think there ought to be? (Laughter.)

Professor Grimshaw: One for each man.

Mr. Charles P. Gulick: Mr. Chairman, I would just like to say a word. Although I haven't had anything to do with Professor Grimshaw's paper I happen to be the chairman of the organization committee of the Sulphonated Oil Manufacturers Association which is now in process of organization. I don't think the textile chemists or the leather chemists realize any more than the manufacturers themselves the chaotic condition with respect to analytical methods, nomenclature, and the other things that we are all forced to deal with.

One of the first things that our proposed association intends to do is to work our proper analytical procedure and nomenclature that will stand the scrutiny of this Association, the American Leather Chemists Association, the Bureau of Standards, and chemists in general.

Our association is being formed with the idea of improving the practices, technical and otherwise, in our industry and as chairman of that association at the present time I want to offer to this Association our hearty cooperation to that end. We hope that in dealing with the sulphonated oil manufacturers this association can deal through our association rather than through individuals perhaps.

We think that in all probability we can get more concerted action with our industry behind our committees in conjunction with your committees.

Thank you.

Chairman Killheffer: I think that is a very good suggestion indeed and I am sure our committee will be glad to bear that in mind.

Professor Grimshaw: Mr. Chairman, I spoke to our President, Mr. Ackermann, and asked him to get in touch with Mr. Gulick in the same manner so he could make an appointment and talk to him about the matter.

Dr. Chapin: I sympathize with Professor Grimshaw in his attempt to say American Association of Textile Chemists and Colorists. I suggest that he take home to our Southern members the suggestion which I think was made by Dr. Stiegler of our local section. We call it A Square T C Square. People here call it the "Society With the Long Name." (Laughter.) I sometimes think it would have a bigger membership if it hadn't so long a name. (Laughter.)

The last paper on our program today is entitled "Two New Scouring Agents," and will be presented by Dr. Meyer of the General Dyestuff Corporation. (Applause.)

. . . Dr. H. Meyer presented his prepared paper . . . (Applause.)

Proceedings of the American Association of Textile Chemists and Colorists

Two New Scouring Agents*

By DR. H. MEYER
General Dyestuff Corp.

SOAP has been the most generally used scouring agent for centuries. It is obtained by saponification of animal and vegetable fats which consist of the glycerine esters of high molecular fatty acids, principally oleic, stearic and palmitic acid, with alkali. In saponification the sodium and potassium salts of the fatty acids are formed, which are soluble in water, but in diluted solution are hydrolyzed in free alkali and acid salts. The salts of oleic acid are the best soluble and also most stable. On this behavior is based the use of soap in scouring and also as a wetting out agent. Of the salts of the fatty acids in technical use only the sodium and potassium salts are soluble in water; the calcium and magnesium salts are insoluble and in hard water a precipitation is formed with soap. The salts of the heavier metals are also insoluble. As to this drawback I shall go into further details later.

Another method to bring fats in a form soluble in water is sulphonation treatment with sulphuric acid or other agents. The first product of this nature was Turkey Red Oil, followed later by higher sulphonated products such as Monopol Oil, Prestabit Oil, etc.; in this group also belong the sulphonated tallows, Neatsfoot oil, etc. These products are more stable in hard water, especially the higher the grade of sulphonation, but in the same degree they lose their properties as scouring agents. The principal use is as wetting out agents and as a medium to impregnate material with fatty matter.

In all these cases the sulphonation takes place in the fatty acid component. In recent research work it now has been found that by transferring the sulphonation to the other constituent of the fat, products are obtained which are soluble in water and besides retain the scouring effect of soap. So far it has not been feasible to get these substances by direct sulphonation, but it is necessary to produce these sulphonated fats in a synthetic way, by making esters from the different fatty acid with sulphonated compounds.

A product of this class is Igepon A, which is now in the market for some time and has found already many friends in the textile industry.

As mentioned before, the calcium and magnesium salts of soap are insoluble in water; in hard water a precipitation is formed. We all know the numerous troubles in the textile and other industries caused by this formation of lime soap. On account of its sticky consistency it is extremely difficult to remove from the material. Most of the troubles in the dyehouse, uneven, streaky and cloudy dyeings, can be traced back to the formation of lime soap on the material. If goods have to be carbonized, the matter is getting worse. It also has to be remembered that in water of say 10° Clark one pound of soap per 100 gallons is made useless by the hardness of the water.

Igepon A, a colorless product of the consistency of soft soap, is readily soluble in water, the calcium and magnesium salts are also soluble; it is absolutely unaffected by water of any hardness, and also not by any metallic salts. Used in conjunction with soap in hard water it prevents the formation of lime soap and it dissolves lime soap formed on the material, even if the goods are dried already. It is in this respect altogether different from other ingredients recommended as addition to the soap bath like Intrasol which transfers the lime soap only in a very fine distribution, which washes out easier; in the case of Igepon A a real solution takes place. In the March number of this year of *Mellian's Textilberichte,* on page 197, a number of very interesting illustrations are given, showing the effect of Igepon A on lime soap.

Igepon A at ordinary and medium temperature is stable in diluted alkaline and even slightly acid solutions. It washes out very easily but even if traces are left in the material there is no trouble to be feared when dyeing, for instance, with acid colors. Soap, as well all know, is very hard to rinse out of the woolen fiber and is liable to give a precipitation of fatty acid. The stability of Igepon A to acid makes it even possible to scour goods of slightly acid reaction without rinsing. Solutions of Igepon A are practically neutral pH value 6.5-7, whereas soap solutions show always more or less alkaline reaction.

One property of soap is missing in Igepon A, it does not act as a fulling agent. This, however, makes Igepon A very valuable for the scouring of piece goods of open texture or fine yarns, knitting and fancy yarns, which are always more or less felted by the use of soap in scouring.

Igepon A may, however, also be used to advantage in fulling as an addition to the soap liquor, as with such an addition even in hard water the full benefit of the soap is assured; there is no formation of lime soap on the mate-

*Paper presented at Annual Meeting, Boston.

rial and the goods rinse very easily and in a much shorter time.

Coming to the principal use of Igepon A in the scouring of woolen material, I do not intend to give you any detailed formulae, as the method of application and the amount of Igepon A vary according to local condition and to the material. I only want to give a few points about the use of Igepon A. Generally, 1½-2 pounds Igepon A per 100 gallons is sufficient to get a good scouring effect. The principal advantage over soap, of course, shows up in cases where no soft or Permutit water is available for scouring; the harder the water, the greater the superiority of Igepon A; but even in the case of comparatively soft water, Igepon A may be used to advantage in rinsing the goods after scouring. In many cases great care is taken to scour wool, especially piece goods, perfectly clean and then the goods are rinsed off in water of a certain hardness. An addition of Igepon A to the first rinsing bath prevents the formation of lime soap on the fiber.

Woolen material, very often from the spinning process, contains free fatty acids. In this case it is necessary to add also with Igepon A, soda ash to the scouring bath to neutralize this acid; the amount depends on the olein contents; generally ½-3 pounds soda ash per 100 gallons is used, a smaller amount for worsteds than for woolen or shoddy yarn. Soda ash and Igepon A should not be mixed in concentrated solutions, but added separately, diluted, to the scouring bath.

In mills near the seashore, the river water and even well water are contaminated with sea water at high tide, which means especially increased magnesia contents and considerable loss in soap. Igepon A will prove very useful in such a case.

Blankets, which very often are dyed with acid colors only, are more safely scoured with Igepon A which does not show any alkaline reaction like soap, the colors do not bleed and the material is kept in a much better condition, open and fluffy.

Pulled wool always contains a large amount of lime and is very hard to clean. With Igepon A it is easy to scour such material, as it is not affected by lime. In cases of excessive lime content 2-4 pints hydrochloric acid may be added to the scouring bath.

A large amount of soap is used in the boiling off of silk. Although Igepon A alone does not boil off sufficiently, an addition of Igepon A to the soap bath procures excellent results.

Besides for scouring, soap is also used to a large extent in the textile industry for finishing, especially cotton dyeings of Indanthren and vat colors, naphthol and sulphur colors. In all these cases Igepon A may be used in place of soap or as addition to the soap bath, to prevent the formation of lime sediments.

As mentioned before, Igepon A is only stable in weak alkaline and acid solutions and not at a higher temperature; but shortly a new brand *Igepon T* shall be available in this market which besides all the good properties of the "A" brand, possesses the advantage that it is stable in neutral, alkaline and acid liquors even at the boil.

This broadens the use of the Igepons considerably. Igepon T will be of great interest as an addition in kier boiling, an ideal disperging agent, not sensitive to lime, long looked for; also in bleaching. In each case the time may be shortened considerably. Igepon T can also be used in any alkaline or acid dyebath to improve the level dyeing and penetration; the dyeings are also of better fastness to rubbing. In this respect Igepon T has proven especially valuable in Naphthol AS dyeing as addition to the naphtol preparation, to the developing bath and also in after-treatment. As you see Igepon T is of special interest to the cotton manufacturer, whereas the "A" brand finds its principal use in the woolen industry.

Although we are here principally interested in the textile field, we must not forget that large quantities of soap are also used as scouring agent in other industries and for domestic purposes. The Igepons on account of their stability in hard water, to alkali and acid, and their neutral reaction and quick action in emulsifying fat, have awakened great interest everywhere. I may mention that the Igepons are already used with excellent results for cleaning of bed feathers, milk bottles, and in the household.

We have in the Igepons, representatives of a new class of chemical compounds which are open to great development.

I have tried only to give you a general idea about the properties and possible use of these products but there is still a wide field open for new applications.

Discussion

Chairman Killheffer: Dr. Meyer says he knows that you want to ask him some questions and he is ready to answer them. (Laughter.)

Mr. C. H. Clark: Can you give us any information on the chemical structure of these products?

Dr. Meyer: There is a possibility of about one hundred or one hundred and fifty different compounds and it is just a question of economics as to which is the cheapest to use.

Mr. Clark: You sulphonate the alcoholic group which may be glycerin, or anything else, and then——

Dr. Meyer: Yes, then make it easier with the fatty acid.

Mr. William Marsden: Dr. Meyer in his paper mentioned Igepon T in connection with Naphthol AS dyes.

I do not want to talk out of turn but I happened to have occasion to experiment with Igepon T to obtain that fastness to crocking which everyone is looking for and I think I can promise that in the future you can save your handkerchiefs more than you did before.

This Igepon T, as Dr. Meyer has stated, can be used in the naphthol prepare as well as in the developer. It can be used in acid liquor and, furthermore, in after-treatment. I used it in small experiments which we have made here. The product itself is not on the market here but reports from abroad are very encouraging and I think for package machine dyeing and for piece goods dyeing we may be able now to produce that desired fastness to crocking which is so essential for heavy shades of the naphthol range.

In giving you a brief explanation in regard to its application I should say that about one per cent Igepon T in the developing bath itself causes a dispersion of the pigment which later on in the boiling soap after-treatment is very easliy removed, much more easily than heretofore.

Furthermore, in the concentrated soap after-treatment, the addition of Igepon, which can be kept very low, goes a long way toward removing the last particles of color lake still sticking to the fiber.

So I can place this produce as soon as it is on the market at your disposal for experiments and I hope you will get good results with its.

Thank you very much.

Chairman Killheffer: Is there anything further on this subject?

Mr. Raymond R. Stevens: Would the use of Igepon A in acid form tend to retard the fulling as it does in soap solution?

Dr. Meyer: We would recommend Igepon T. It wouldn't retard it. It would accelerate it.

Mr. Stevens: Would it tend to clean your goods? In other words, in acid fulling the goods do not tend to clean up. Would there be any advantage in introducing it in an acid fulling solution?

Dr. Meyer: Yes, it has been tried out abroad and with very good results.

Mr. Stevens: How strong a solution of acid could you use and introduce the Igepon? The T would be preferable?

Dr. Meyer: It would be absolutely stable.

Mr. Stevens: And it would not retard the fulling?

Dr. Meyer: No. In fact, it would accelerate it.

Mr. Stevens: In other words you can still depend on the acid to full your goods down?

Dr. Meyer: Yes.

Chairman Killheffer: Is there anything further? It looks like you are getting off easy, Dr. Meyer. (Laughter.) If not, I guess it is in order to adjourn to our several rooms.

. . . The meeting thereupon adjourned at five o'clock . . .

Purchasing Products and Selling Results*

By PAUL F. HADDOCK

Southern Manager, A. Klipstein & Co., Inc., Charlotte, N. C.

MR. CHAIRMAN, Members of the Piedmont Section, of the American Association of Textile Colorists and Chemists, and Guests:

About two weeks ago, yours truly happened to be dining in the Poinsett Hotel, in Greenville, South Carolina, when in came our Vice-Chairman, Jack Crist, looking like he had just had a 10 per cent cut in salary, lost a large contract on account of price cutting, and worried about the condition of Joe Moore, all at the same time. I said, "Come on over, Jack, and join us. You're just in time to match for the check. Sit down. Tell us all the news. And, by the way, what made you go on the wagon?" Well, after Jack got through explaining why he had to quit drinking, he opened up and told me his real trouble. Jack had to get a program ready for this meeting and he had no speakers, papers, or what have you. I told Jack not to worry, anybody could "get up" a paper. Then Jack's eyes grew bright, and his face lit up with a beautiful light, and he says, "Paul, did you ever hear about the black hen that laid the white egg?" "Sure," says I. "There's nothing to that." "Well," says Jack, "Can you do it?" Say, fellows! I'm telling you, I felt just about as small as the individual from Fort Mill, who came up here and said he could whip any man in Charlotte—after regaining consciousness, he realized he had taken in too much territory. And so did I,—I had to accept.

The subject Jack assigned to me was that of "Purchasing Products and Selling Results." I said, "Listen, Jack, I haven't forgotten the excellent address Mr. Hill Hunter gave us in Greensboro entitled "Purchasing for Textile Mills." And the very next meeting Mr. R. E. Sumner presented a paper entitled: "Selling to Textile Mills." And now you want me to talk about both buying and selling. Comparatively, there is no buying, and there is no selling—all we do is talk about it! I feel somewhat like the old maid, seventy years old, confessing to the priest, saying that she had been a naughty girl, and the priest saying, "When was this?" "Fifty years ago," says she. "But," says the priest, "Haven't you confessed about

*Paper presented at Annual Meeting of Piedmont Section.

this before?" "Sure," says the old maid, "But I still love to talk about it."

Probably, some of you gentlemen are wondering what Paul Haddock knows about purchasing. Let me tell you. For the last twenty years, I have made a fairly good salary, and, after Uncle Sam got his share, I spent the balance. I guess I know quite a little about purchasing. All a purchasing agent does, is spend part of somebody else's money—while I spent all mine! And I can see some of you wondering what Paul Haddock knows about selling. Listen! I used to know quite a little about selling, but, for quite some time I have been getting lessons on how to *give* MERCHANDISE away. However, I thank God that condition is about over.

According to the Bible, buying and selling originated in the Garden of Eden. Adam had a fine idea that he wanted to sell Eve. He must have been quite a salesman, and Eve must have been quite a purchasing agent, otherwise, I'm afraid we would have had no salesmen, or purchasing agents today, and none of us would have been here tonight.

One of the greatest purchasing agents the world has ever known, was also mentioned in the Bible—this was Joseph. During the Seven Years of Plenty, Joseph bought all the corn there was in Egypt, to take care of the Seven Lean Years to follow. So you will see that Joseph bought wisely and well. However, if he was on earth today, due to change in conditions, he could not buy one per cent of all the corn made in North Carolina alone.

The Bible also tells us there are certain ethics in buying and selling. Jesus Christ threw a bunch of salesmen out of the Temple at Jerusalem for selling pigeons on the Sabbath. This may explain the peculiar fact why salesmen do not work on Saturday (the Sabbath of the Jew, the world's master salesman) nor on Sunday, the Sabbath of the God-fearing purchasing agent. It was this same Jesus, who promulgated the Golden Rule, the greatest guide to salesmanship the world has ever known: "Do unto others as you would have them do unto you." David Harum, however, reminds us of the modern version. Harum said: "Do unto others what they would like to do to you, but be sure you do it first!"

Let us go back and review what Mr. Hunter had to tell us in Greensboro, at our last January meeting. The more and more one reads that address, the more and more sound and vital his remarks appear to be. You will remember how nice Mr. Hunter was to the traveling men? He referred to them as "Commercial Ambassadors"—and I suppose you are all familiar with the names they use, when referring to one another. At this meeting Mr. Hunter stated as follows: "A first-class chemist, and a laboratory, is the buyer's right hand in successful dye buying." Mr. Hunter further stated: "I feel that every plant should maintain a competent research department. It remains a very definite fact that it costs any mill lots of money not to have a department of this character. When you think of the large number of items that go to make up a manufactured product, it is easy to see the necessity for constant investigation of the items best fitted to the given conditions, that is, those that can be most economically used, and in this day of thin profit margins, if any at all, the necessity of finding satisfactory and less costly things to substitute is obvious, and the only way I know to do this successfully in a large way, is to maintain a department that is constantly on the lookout, and making constant experiments, in order to ascertain what can be used under any given conditions to a maximum advantage."

We will now go back and see what Mr. Sumner had to say in Greenville last April about "Selling to the Textile Industry." Here it is—Mr. Sumner chose his remarks very well in the following statement: "The sales cycle of any technical product is very long. It takes a long time to get tests. I, of course, realize that the customer has a lot of things to do except test goods, but that can be speeded up, and it will be just as good for the buyer as it is for the seller." Mr. Sumner also quoted: "In selling a technical item, it is the responsibility of the sales department to provide a competent technical organization to properly service their goods. You have got to spend a lot of time and a lot of money in finding out how their goods work, under what conditions they work, and how they will fit particular needs, and all that sort of thing. This is highly important, from the point of view of the seller as well as the buyer. It is obviously to the best interest of both to see that the goods, which are sold and purchased, work as efficiently as possible." And he concluded with the statement: "We know—that millions of dollars are saved, simply by substituting one product for three, and it is only by the very close working together of the buyer and the seller that this is at all possible. They can be responsible for the development of better and cheaper ways of doing today's job, and can prepare their respective companies for them tomorrow."

Now, gentlemen, I desire to make myself perfectly clear when I state that I am absolutely in accord and positively honest in my conviction, in saying that I fully agree with all Mr. Hunter and Mr. Sumner said in the above extracts from their remarks. However, since the subject of my paper is: "Purchasing Products and Selling Results" it becomes necessary on my part to carry their ideas still further.

For instance, Mr. Hunter says: "A first-class chemist and a laboratory is the buyer's right hand in successful dye buying." I think this same thing also applies to the correct purchasing of oils, softeners, sizing compounds, waxes, gums, starches. Aye! and even chemicals. Mr. Hunter next stated: "I feel that every plant should main-

tain a competent research department" and so on, but I would like to know how many textile plants maintain a competent research department, and I think that I am safe in my assertion that any one of the large American or European dyestuff manufacturers spend more money on research than all the bleaching, dyeing, mercerizing, printing and finishing plants in America. Mr. Sumner says: "The sales cycle of any technical product is very long." And why is it long? It is simply because the average plant, not maintaining a research department, is not in possession of the knowledge that will promptly allow them to switch from one technical item to another.

Mr. Sumner states again: "In selling a technical item, it is the responsibility of the sales department to provide a competent technical organization to properly service their goods." And I would like to add that if the plants consuming these said technical items will also provide a competent technical organization, they, too, could properly service their plants. Mr. Sumner again said: "We know that millions of dollars are saved simply by substituting one product for three." I would like to add to this, that millions of dollars could be saved, providing sufficient technical knowledge was available in all the plants, in order to make a correct economic substitution an immediate possibility.

Suppose we take the major chemical and technical operations employed in textile plants; these would roughly sum up as follows: Sizing, bleaching, mercerizing, coloring, and finishing.

First take sizing: We all know this has been much cussed and discussed. Let me ask you why is it that no definite universal procedure has been adopted to produce definite desired results? We find the incorrect selection of starches and gums; the indiscriminate use of animal, vegetable and mineral greases, embracing solubles, emulsions and insolubles; the dangerous use of chlorides instead of correct deliquescents; the weighting of warps that go into fabrics that have to be subsequently bleached or dyed and some times the sizing of warps, so-called pure, when weighting would be advisable for the export trade. And in many plants we find warps are sized and the goods manufactured with absolute disregard of the subsequent chemical operations by which these goods are likely to be processed.

Second take bleaching: Let me ask you why is it we find that bleachers desize with acids, enzymes, water steeping, and, in lots of cases, not desizing at all? Why is it we find bleachers with sufficient water and physical equipment at their disposal using peroxide when the chlorine process would be more economical, and on the other hand, we find bleachers of goods containing colored patterns still fooling with chlorine when they should have been on peroxide years ago? And we still find bleachers giving goods two, three and even foud boils where it isn't at all necessary. And we still have the diversification of ideas with regard to scouring agents.

Third take mercerizing: Let me ask you why is it the same goods are mercerized sometimes before bleaching and sometimes after bleaching? Why some mercerizers process in the presence of the natural oils in the fiber, while others completely eliminate these oils? Why, in the finishing of mercerized yarns, softeners are used to improve their quality as to the adaptability for knitting, without due regard to the possible trouble that may be encountered in the subsequent dyeing operations?

Fourth take coloring: Let me ask you why is it we find in many instances colorists employing such a wide variation in physical equipment, endeavoring to process the fiber or fabric by one method, when the result they are trying to duplicate has been obtained in an entirely different manner? Why is it we find colorists trying to get away with inferior colors and on the other hand, colorists wasting money on high priced types and methods, where correct substitution would be economical?

Fifth take finishing: Let me ask you why is it we find no two plants endeavoring to produce the same finish, on the same fabrics, and in many instances for the same customer, not even using the same physical equipment nor even similar finishing materials? And why is it, that 90 per cent of the finishers, all over the world, are still employing the same processes and products as their fathers before them, yes! and even their grandfathers? Confidentially, the greatest blessing in disguise to me, was the losing of my late grandfather's treasured formulas, necessitating research on my part which resulted in my establishing more economical products and processes.

Gentlemen, it appears I have used the question "Why is it?" several times, when in reality I am not supposed to be asking you; I am supposed to be telling you. So here goes! I'll tell you why. It is due to the fact that most plants have backed up the purchasing agent with a laboratory and chemist for the testing of products alone, without furnishing their organization with a research or plant chemist to check the processes. It is because the average plant foreman knows what he knows, but not all he ought to know, about his own business. It is because many purchasing agents (and this covers managers, superintendents, and all others who buy or decide) tell you they don't want to change. That is a lot of "bunk!" They do want to change. The truth of the matter is, they're afraid to. It is because technical men, representing companies merchandising technical items cannot in most instances, be received by similar technicians competent to discuss worthwhile economy. And it is because every once in a while we run into that brilliant dumbbell, who claims he is "satisfied." What a laugh that is. "Satisfied!" Who is satisfied these days? The only satisfied persons I know of are those who are not in

business at all, having their accumulations tucked away in gilt edged securities, and that "satisfied" person, ignorant as the Devil, who is a fit subject for the insane asylum. Imbeciles are always satisfied. But listen! Don't think I am jumping on the purchasing agents or the buyers. The average purchasing agent in the South is a very high type of gentleman and very friendly to the traveling man. Only the other day I saw a quotation by Emerson, on a purchasing agent's desk, reading as follows: "Life is not so short but that there is always time for courtesy." And that is true. It's easy to get in, but likewise it's easy to lose out. The point I want to bring out, however, is that we are selling results and the mill is buying and selling results, too, or, I should say, endeavoring to do so, but through lack of information which prevails due to the absence of research organization, the purchasing agent's hands are tied, and he has to purchase a product, rather than a result.

Let me mention a few of the major products. We will take first:

Starches. The total consumption of starch in the textile industry amounts to more in tonnage and money (not in one plant, but in the textile industry as a whole) than all the dyestuffs and chemicals put together. Here we find that starch manufacturers are employing chemists of the highest possible calibre, while on the other hand there is actually less known about starches by the consumers than any other chemical or raw material entering into their products and processes. There is not only little known about starches, but daily we find in addition to the lack of information, a fund of misinformation. I grant, that if a man uses corn starch, he is familiar with corn starch and the same thing might apply to potato starch or wheat starch, etc., but it might be surprising to tell you, that due to conditions abroad, this is the first year in the history of my experience that tapioca flour is selling cheaper than corn starch—and I mean cheaper than the cheapest corn starch. Forty million pounds were imported from Java into the United States in the first three months of 1931, and what happened? The large mills and the purchasing agents who had a technical organization to back them up, were quick to take advantage of this golden opportunity! While on the other hand, nine out of every ten men operating small units not so fortunately equipped, never even heard of tapioca flour at all and even those who had, couldn't tell you how to boil it.

We will next take softening compounds: God alone knows how much money has been spent and how much money has been wasted on these articles, purely and simply on account of the lack of information. I know, and you know, that if a plant chemist was employed Mr. Bleacher Mr. Dyer and Mr. Finisher would not be in a position to tell the purchasing agent that Mr. So and So's "so and so" would do the work and nothing else would answer his purpose. Many of these articles are specialties, but specialties under mass production become staples. And, with all the "hooey" left out, there is absolutely no reason why they cannot be manufactured and sold by reputable firms at a fair margin of profit. But this will never take place in a general or universal way if the buyer is restricted to the purchase of a product rather than a result.

We will now refer to dyestuffs: Colors are the most intricate and interesting of all manufactured chemicals. Here we find that practically all sellers have staples and a good number of specialties at the same time. But when it comes to colors, it seems to me at the present time that all the purchasing agent can do is buy what the requisition calls for. The laboratory chemist is there to see that the shipment is up to sample or one shipment checks against another, as the case may be. We all know of lots of plants where economic substitution could be effected, provided there was a connecting link between the actual dyer and the purchaser. Products, processes and local conditions enter largely into this branch of industry, but in lots of cases better results can be accomplished; time can be saved, and economy put through, provided the technical men of the dyestuff companies could, in addition to interviewing the purchasing agent, come in contact with the plant chemist who is working in close co-operation with the dyer and capable of adopting the salesman's wisdom, should same be found logical.

The same thing applies to chemicals: Chlorine ran chloride of lime out of the market, but it wasn't sold as a product, it was sold as a result! The same thing applies to SO_2 gas. For instance, where the operation and conditions permit, what's the use of buying hydrosulphite of soda powder if zinc and bisulphite will suffice? And then again, what's the economy in buying bisulphite now that you can buy SO_2 gas?

I am a little afraid that this paper of mine is running into lengthy proportions. The next speaker on the program will be much more interesting, he being from Washington, and may have a word of cheer—telling us that we are going to make lots of money in 1932 in contrast to my advocating stringent economies in 1931. But before closing I would like to bring a message or a new thought before the Piedmont Section of the American Association of Textile Colorists and Chemists.

What the southern textile trade needs today is more Harold Chases, John Simmonses, George Feindells, and others of the same type.

You fellows ought to realize that there is much more money in brains than in barrels, provided the brains are properly applied. What I would like to see is the laboratory chemist retained for the checking of purchases and maintaining of standards. Competition alone practically insures this, but when competition gets to keen, you need to be doubly sure that the standards will be kept up. But,

in addition to this, I contend that all plants should employ plant chemists, and where this Association would fit in, is for all the members to become salesmen, selling themselves together with results to the textile trade. There is a lot of talking every day about unemployment but there is also a lot of golden opportunities awaiting men of the right calibre. These men should be the "go between" connecting the purchasing agent and the plant foreman, and they could and should determine how best results can be purchased.

I don't want to be accused of blowing my own trumpet, but as an example of the possibilities in the textile trade awaiting the brains of this Association, I hope you will pardon me if I point out one specific instance in a plant where I recently had the privilege of doing some experimental work on economizing. This plant had always maintained an efficient chemist, but his time was being wasted—he was analyzing products instead of processes. We got together; went through his formulas and, by substitution of worthwhile raw materials in the place of a lot of "junk," I was able to show them a saving of an eighth of a cent per yard. An eighth of a cent per yard, in a plant doing five million yards per month, means $75,000 per annum, or seven and one-half per cent on a million dollars.

What we need today is not the type of salesman bragging that he could sell a baby buggy to a bachelor.

What we need is not the grid-bar type of salesman, telling us that a set of his bars would save 90 per cent of coal and leading us to believe that with two sets we would need no coal at all.

What we need is not the messenger-boy type of salesman; asking for information instead of dispensing information; wasting his own company's money together with the valuable time of a purchasing agent.

What we really need is men who can guide us from the Rule-of-the-Thumb methods of the past into the scientific fields of the future; men of instruction, construction and determination. The whole world is now mourning the loss of the *one* man who had all the qualities I have mentioned; the one who gave light unto the world; the one who by his vision, research and determination, created new industries capitalized at over fifteen billions of dollars. We can't all become Edisons, but we can, in a measure, be guided by the greatest scientist of modern times, the one who was never satisfied to accept methods and conditions as he found them. The late Teddy Roosevelt said of leadership: "With ordinary talent and extraordinary determination all things are obtainable." Mr. W. S. Lee, Sr., the recognized head of the Southern Power Company and president of the American Association of Electrical Engineers, said: "The way to success is to do a common thing in an uncommon way."

Scientists, chemists and efficiency engineers have been accused of being responsible for the depression, by creation of over-production, but I contend that if the brains of the world got us into this Hell-of-a-mess it will be the same brains turned into economists, that will solve our problems and get us out again.

"When it comes down to the question of the hardest shot to make
It depends upon conditions and what there is at stake.

Most any dub can hit a ball in tennis, golf or pool,
Whene there's nothing up at all and he is calm and cool.

It's when the going's getting rough that the few can leave the mass;
And the ones who really have the stuff, begin to show their class.

Of all the shots from tee to green that allow for no mistake,
The hardest one I've ever seen is the one *you have* to make."

The Physical Chemistry of the Proteins of Silk and Wool

(Continued from page (62) 82)

harm to the silk. At about pH 10 you have approximately ten thousandth normal alkali. That has been found by trial and error to be a very good place to boil off silk and you are far enough away from the iso-electric point to make the sericin fairly soluble. At pH 12 it would be more soluble but at that pH you would start doing damage to your silk. You can very readily see if you go to the acid side of the iso-electric point and go down to approximately pH 2 where the sericin will still be comparatively insoluble, you will be down to tenth normal acid. I would predict that satisfactory boil-off could not be obtained using acid solution because if you get far enough away from the iso-electric point to dissolve the sericin, the solution will be strong enough in acid to do considerable damage to the silk.

AMERICAN DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

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WHAT SEQUEL TO THE DYE CENSUS?

WHY did the U. S. Tariff Commission discontinue the dye census? What chance is there for restoration or replacement of this annual inventory of production? These questions, or others to the same end, have been asked repeatedly, during the past few weeks, by members of the dyestuffs industry who seek the news behind the news.

Judging from the letters which have come to Washington, the industry was not wholly conscious of how much it had come to depend upon the compilations by the Chemical Division of the Tariff Commission until announcement was abruptly made of discontinuance with the publications of the final figures for the calendar year 1930.

Going behind the conventional announcement by the Tariff Commission, we find three separate and distinct reasons for the termination of this unique undertaking. The first reason consists in the fact that the job for which this special census was called into existence is done and, if the original authorization be narrowly or literally interpreted, there is no justification for prolonging the statistical work. As our readers know, the Dye Census was established incident to U. S. tariff legislation to demonstrate the capacity of a tariff wall to foster, within a set period, an infant industry. The prescribed term has long since expired. The Census was prolonged for a time because the dye industry desired it. But, latterly, the changing circumstances affecting this and all other phases of Governmental research work brought to the Tariff Commission a feeling that continuance of the Dye Census was not warranted without a renewal of the mandate from Congress.

The second reason—intimately related to the first—is found in the economic situation as reflected in the Federal deficit. The Tariff Commission, in common with the other departments and independent bureaus of the Government is, at the command of the Budget Bureau, paring expenses in every direction. The necessity for retrenchment, combined with the circumstance that the Dye Census had already overstayed the period of its invitation, served to mark this project for sacrifice. Officials of the Tariff Commission have stated for the REPORTER that they have enjoyed conducting the serial survey of the dye field and would have been glad to continue it did they not find their hands tied.

The third reason for discontinuance might have operated sooner or later as solely sufficient had there been no question of Congressional intent or of provision in the Budget. This third factor consists in a growing display of jealousy on the part of other industries that would like to share in the facilities that have been enjoyed by the dye industry. Not one but several industrial groups have raised, with the Tariff Commission, the question of why, if dye production was specially censused they should not have similar tabulations for their respective lines. As these pleas have grown more insistent, the tariff commissioners have found it difficult to deny to tobacco, steel alloys and other commodities the service that has been accorded to dyes for more than a decade past.

Facing interruption of the Dye Census as an accomplished fact, what can be done about it? Is there any chance of securing a resumption,—perhaps in time to yield 1931 figures in October next, even if there could be no report of preliminary figures in April of this year? Frankly, the prospect is not encouraging. The obvious solution would be to obtain a renewal of the grant from Congress. But with the primary object of the dye census clearly attained and in the present state of the public finances this is a long chance. To be sure the measure now pending in Congress affecting the powers of the Tariff Commission does provide an opportunity for inclusion of special authorizations, if unopposed, in the form of a rider. But the prospect is not good that such a course would avail in the case of dyestuffs.

Inasmuch as the cost of the service has been an important obstacle to the continuane of the Dye Census it has occurred to members of the industry that the program might be continued under Federal auspices if money were found at outside sources to cover the actual costs. To that end, representatives of the dyestuffs industry have offered to collect and turn over to the Tariff Commission, from contributors within the industry, an annual fund sufficient to meet the expenses of the survey. There is a precedent for this in the cooperative arrangements between various industrial groups and several different research agencies of the Government, as, for example, the association in research participated in by the American Association of Textile Chemists and Colorists and the National Bureau of Standards.

A difficulty arises, however, in the case of the Dye Census. Partnerships, such as the one above mentioned, are feasible, and are encouraged in the case of administrative branches of the Government. But the situation is different in respect to the Tariff Commission which is

judicial rather than administrative in function. Yet would it simplify matters if the Tariff body could continue the project not merely because it has a background of experience and a trained personnel but likewise because it has been able to summon the element of obligation in securing returns which has been in considerable degree responsible for the success of the Dye Census?

One enthusiast has suggested that it should be possible to persuade Congress to transfer from the Tariff Commission statutes to the measure making appropriations for the Department of Commerce, the paragraph requiring dye producers to report production. Lacking the note of Federal demand, which has heretofore insured 100 per cent coverage, the industry-financed, Government-administered dye census would be dependent upon the fullness of the spirit of service within the industry. Presumably the Department of Commerce would not participate, even with expenses paid, unless there was assurance that at least 85 per cent of the industry (in terms of production capacity) would regularly cooperate. This quota has been demanded by the Federal Trade Commission in connection with its Trade Practice Conference agreements and by the officials of the Simplified Practice Division at the National Bureau of Standards when assisting an industry, at its own request, to frame recommendations for standardization of colors, sizes, etc.

One other possible recourse remains and that is the Bureau of the Census Dye production is, of course, already dealt with in the Census of Manufacturers. But two limitations upon that record of production have restricted its value to the dye industry. First, the Manufacturers Census is taken biennially instead of annually. Second, the time that elapses before publication of the results disqualifies the Census returns as a guide to readjustment of policies in the dye industry to conform to current conditions.

The fact remains, however, that for all that the dye industry has not had the benefit, the Census Bureau has facilities for turning around quickly enough on special compilations. For example, at monthly intervals the Census Bureau publishes statistics relating to cotton supply, consumption and distribution. Similarly, monthly or quarterly statistics are collected regarding the production or supply of many other commodities including hides, skins, leather, clothing and wool. The mere fact that exception has been made in favor of textiles would seem to supply a precedent that might be used to persuade the Government that it was desirable to have the Census organization undertake the compilation of figures on dye production and distribution, annually if not quarterly.

By WALDON FAWCETT

EDITOR'S NOTE— In connection with the foregoing editorial it is interesting to note that the Synthetic Organic Chemical Manufacturers Association of the United States at its January meeting directed that they go on record as regretting the discontinuance of the publication of the Census of Dyes and Coal Tar Intermediates for 1931 and urging its resumption for 1932.

Garvan Eletced President

Francis P. Garvan, president of the Chemical Foundation, Inc., was elected president of the United States Institute for Textile Research, Inc., at a meeting on January 22nd at The Chemists' Club of the latter's Board of Directors. He succeeds the late Dr. Samuel W. Stratton who was the first president of the Institute. The nomination committee that prevailed upon Mr. Garvan to head the Institute consisted of H. V. R. Scheel, Chairman, Dr. E. H. Killheffer and Philip A. Johnson.

Mr. Garvan is a Yale graduate and an attorney-at-law by profession. During the World War he was head of the Bureau of Investigation of the U. S. Department of Justice, and assistant attorney general under attorney-general Palmer. He succeeded the latter as Alien Property Custodian, and in this capacity and later as president of the Chemical Foundation, he was one of the chief factors in making possible the present great chemical and dyestuff industries in this country.

The Chemical Foundation was "chartered for the advancement of chemical and allied science in industry in the United States," and the textile industry is one of the largest users of chemicals and dyestuffs. U. S. Institute of Textile Research is engaged in promoting scientific research for its industry. Both are non-profit organizations. In the chemical research field these organizations are complementary to a considerable degree, and Mr. Garvan brings to U. S. Institute an intimate knowledge of the textile industry's chemical research needs, and also great ability as an administrator and organizer.

Courses in Textiles

Two evening courses which will start with the second semester at Columbia are "Course on the Manufacture, Weaving, and Converting of Rayon and Other Synthetic Yarns and Piece Goods" and a "Course on the Dyeing, Finishing and Printing of Cotton Goods." The instructor in these courses will be Herbert R. Mauersberger, graduate of Lowell Textile Institute and formerly of Cox, Fuller, and Mauersberger, consulting textile specialists. The fee for each course will be $20. The first course mentioned above will start on Thursday evening, February 4th, and the second course will start on Friday evening, February 5th. Bulletins concerning these courses may be obtained from the University.

Survey of Textile Research

Copies of the "Survey of Textile Research in the United States" conducted for the Textile Foundation, Washington, D. C., by the United States Institute for Textile Research, Inc., are now in the process of distribution. This survey is a very complete summary of textile research in the United States and represents a great deal of effort in gathering and compiling the statistics. Copies of the survey may be obtained from the Institute at 65 Franklin Street, Boston, Massachusetts.

Colloidal Aspects of the Dyeing of Wool With Acid Dyes

(Continued from page 72)

wool fiber and the dye in the following manner (American Dyestuff Reporter 18, 148, 1929).

(Here Bancroft has drawn his conclusions from observing the curves resulting when a dye is absorbed from solution by the fiber. The writer has shown these in Figure 1.)

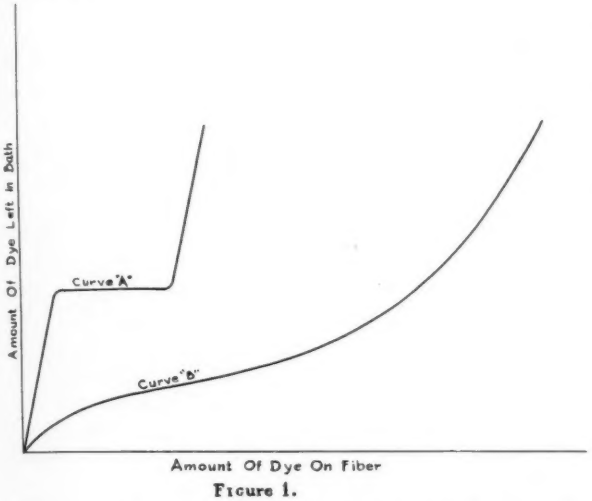

Figure 1.

"If the dye were forming a definite chemical compound with the fibre, you would find a curve that ran first vertical, next horizontal, and then vertical again. (Curve A in Figure 1). ....., and the concentration in the dye bath would remain constant while the amount of dye taken up would vary. This happens in all cases where you know you have compounds. This does not happen in dyeing, for if you vary the concentration in the dye bath with every single dye you get a continuous variation in the amount of dye taken up. That is, you get a smooth curve (Curve B, Figure I)."

Bancroft bases his theory on the postulation that a fibre tends to adsorb everything in the dyebath in amounts varying with the nature, concentration and temperature of the solution and with the nature of the fiber.

In the case of acid dyes in acidified baths, these constituents are hydrogen ions, sodium ions (if dye is sodium salt), anions of the dye, anions of the acid, and undissociated compounds. The hydrogen ion being more strongly adsorbed than any univalent cation will be taken up largely, and the fiber will thereby become positively charged relative to the solution. The positive charge, in turn, will lead to an increased adsorption of anions, and by this secondary process of adsorption, the charge on the fiber will become more or less neutralized. Since in being adsorbed, the anions of an acid dye have to compete with the other anions of the bath, it follows that the addition of other strongly adsorbed anions will decrease the amount of dye taken up. This is found true when the strongly adsorbed sulphate ion is present upon the addition of Glauber's Salt to the bath. Thus a restraining action on the dye ensues.

In a similar way, the addition of a strongly adsorbed cation will increase the amount of dye taken up, other factors remaining constant. This occurs when upon the addition of the hydrogen ion of an acid, greater absorption of dye is effected.

Thus from a colloid standpoint, we have the explanation for the dyeing of wool by acid dyes from acidified baths. Yet little has been stated by investigators in explanation for the property of a number of acid dyes of possessing an excellent affinity for wool from a neutral bath. One explanation forwarded is that the color acids of these dyes are freed even in neutral solutions, and these exert the dyeing action. This theory, however, has its weak points.

In practical dyeing, neutral dyeing acid dyes are applied to the greatest extent to cotton-wool union fabrics by the one-bath process, in which the wool is dyed by this class, and the cotton colored by those substantive dyes which possess little affinity for wool even at the boil. In this operation, the practical dyer disregards theory, when in the event that the shade of his wool is weak, an addition of Glauber's Salt is often made to throw more of the neutral dyeing acid dye from the solution on to the fiber.

The effect of this procedure can be check, if two 2% dyeings are made on wool of Alphazurine A (Colour Index No. 714—Schultz No. 545) which is a neutral dyeing acid dye of the Patent Blue family; one dyeing containing no Glauber's Salt and the other, 20% of Glauber's Salt. It will be noted that the wool dyed in the bath containing the Glauber's Salt, possesses a much heavier shade than that dyed with the dye alone.

Thus the Glauber's Salt here acted not as a retarding agent, but as an exhausting agent instead. This is, however contradictory to the theory of dyeing acid dyes from acidified baths.

In working with certain acid dyes on wool which possessed good fastness properties in all respects, the writer was struck by the unusual action of these dyes in behaving not unlike substantive dyes. It may be well to

state at present that these dyes possessed great affinity for wool from acid dyebaths, so much in fact, that the weakest exhausting assistant had to be employed for level results, i.e., ammonium acetate.

Their similarity to substantive dyes existed in their property to assume a turbid condition soon after 1% stock solutions were prepared, a characteristic displayed by typical substantive dyes like Benzopurpurine 4B (Colour Index No. 448—Schultz No. 363). This would tend to indicate a condition of greater molecular aggregation at lower temperatures, a property of many colloidal dye sols.

The writer decided to select one of these dyes, Polar Orange R (No Colour-Index Number), and note its behavior with wool from neutral solution.

A 2% dyeing for 30 minutes at a boil showed a marked affinity of the dye for the fiber, and a similar dyeing with the addition of 20% Glauber's Salt produced a much heavier dyeing. This was a characteristic of a typical neutral dyeing acid dye.

When a 1% solution of the dye was subjected to an electric flow for eight hours, it was found to be electro-negative, like most substantive dyes which have been shown by cataphoresis tests to be electro-negative in solution.

At this point, we suspected that the dye might not be present in neutral solution, as a true solution but might exist as a colloidal sol. Consequently, it was decided to note its affinity for cotton, since we realized that cotton is dyed with reasonable fastness by only those dyes which are present in solution as colloids. In experimenting with basic dye solutions (Melliand 2, 11, 1931) we had succeeded in reversing one of these dyes from true to colloidal solution, and in this manner were successful in dyeing viscose directly, without a mordant, with fair fastness.

A 2% dyeing of the Polar Orange R with the addition of 20% Glauber's Salt was therefore made on cotton, and the affinity of the dye for the fiber noted. There was a marked affinity with excellent exhaustion of the dyebath. The dyed fiber exhibited fair fastness when subjected to a washing test, the fastness in this respect being comparable to certain substantive dyes.

A neutral dyeing of the acid dye was then made with the addition of Glauber's Salt to a piece of cotton-wool union goods for the purpose of comparing the relative affinities of the dye for cotton and wool from a neutral bath. A fairly good union dyeing was produced, the wool being dyed slightly heavier than the cotton.

To further test for colloidability in neutral dyeing acid dyes, 1% solutions of two of these, Alphazurine A (Colour Index No. 714—Schultz No. 545) and the Polar Orange R (No Colour Index No.) were prepared. Another 1% solution of an acid dye which showed marked affinity for wool only from an acid bath, Tartrazine (Colour Index No. 640—Schultz No. 23) was also prepared. A few cc. of 10% H_2SO_4 solution were added to the latter solution to lend acidity to it. The diffusion of these solutions into a gum tragacanth gel was then noted.

The Tartrazine diffused immediately and quite rapidly. There was little diffusion on the part of the other two dyes, and after twenty-four hours, the total extent of diffusion was small.

When Bancroft formulated his adsorption theory of the dyeing of acid dyes on wool, he dwelt but little on the theory attached to the action for the dyes of the neutral dyeing class. From the above few tests, some insight is gained as to an explanation for the behaviour of neutral dyeing acid colors on wool. It appears that the action of these dye solutions are similar to colloidal dye sols, like substantive dyes, in many respects. In the few solutions observed it appeared that the addition of an electrolyte destablized the solution and caused greater adsorption by the wool, the latter behaving in this case much like cotton.

In discussing the theory of dyeing wool, Bowman (Structure of Wool Fiber, Macmillan, P. 108, 1908) attempted to explain the versatility of this fiber by stating that with a more complicated molecule the greater was its affinity and because of its greater atomic heterogenity, wool offered more points of attack, and more links in its atomic chain where attachments might be found. This, indeed, may apply to the activity of the wool in its affinity for colloidal dye sols.

The best explanation for the behaviour of neutral dyeing acid dyestuffs as demonstrated in the experiments conducted by the writer, is that contained in a study of the physical chemistry of dyeing by Briggs and Bull (Jour. Phys. Chem. 26, 845, 1922). These are contained in the following conclusions of these investigators:

(1) The adsorption of acid dyes by wool is a strictly adsorption phenomenon.
(2) All dyes behave like substantive dyes if their solution becomes colloidal. For this reason, Methylene Blue, as soon as it has been rendered colloidal acts like a substantive dye and no longer behaves as a true basic color.
(3) The restraining effect of sodium sulphate on acid dyes may pass through a maximum as the sulphate concentration is increased. Dialysis experiments have shown that the higher adsorption of an acid dyestuff (in the presence of the sulphate ion) was due to a decrease in the solubility of the dye.

Coincidental with the above conclusions, the writer opinions that many acid dyes in neutral solution exhibit colloidal properties, and in this state behave much like substantive dyes. An addition of an electrolyte, like Glauber's Salt, causes a destabilization of the dye solution and causes a greater exhaustion of the dye.

However, it appears that the molecular condition of these dyes is such that the dye aggregates may be of smaller size than that of substantive dyes. This would be the exact antithesis of colloidal basic dyes, whose molecular condition, the writer found, was such that even the less colloidal sols existed in a high state of colloidability with rapid coagulation by the addition of electrolytes.

An Introductory Study of Textile Microbiology—Chapter V

By **WILLIAM G. CHACE**

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This is the fifth in a series of articles on Textile Microbiology. The four other installments have appeared in preceding issues of the Reporter. As explained by the author the purpose of these articles is to enable the textile chemist or other laboratory worker not trained in microbiology to learn the essentials or enough of the technique to personally undertake work in this field.

THE extreme importance of working with pure cultures, or possibly with mixtures of known organisms, cannot be too strongly urged on the worker in this field. As already stated in a previous article[25] much of the work of the early investigators of textile microbiology must be regarded as practically valueless because the cultures they used were obviously irresponsible mixtures. The properties of the various organisms, even those in the same class, differ so much that work carried out on an unknown mixture can hardly be considered as having any value. This fault has been particularly noticeable among workers investigating methods of mildew prevention.

Isolation in pure culture is comparatively easy for most of the organisms causing mildew, where the extreme difficulties encountered in obtaining pure cultures of soil organisms do not usually appear. In order to obtain any organisms in pure culture, it is necessary to get one single organism alone and collect its descendants. This has been done microscopically, but the process is very difficult and tedious and requires special apparatus and too complicated a technique to go into here. A very ingenious method of obtaining single mold spores is occasionally used. It consists of making a suspension of the spores in sterile water and diluting this suspension until the drop carried by a loop in the platinum needle sometimes carries single spores. A series of drops is then placed with this loop in a row on a sterile microscope slide, and each drop examined microscopically until one is found which contains a single spore. This drop is transferred to medium and allowed to develop. The difficulty in this technique lies in the fact that many, many drops must be examined before one is found that contains a single spore. There is a further disadvantage in that there is always the chance that the particular spore chosen may not be of the principal infection.

The usual method of obtaining pure cultures is to get a single organism or spore on a plate of solid medium in a Petri dish and allow it to grow there until a colony large enough to be seen with the naked eye has developed. This method is quite easy and allows the selection of several different organisms from a mixture. It also gives some idea of their relative numbers. Applied to textile materials it may be done as follows: The material to be investigated is transferred, with aseptic precautions, to a tube of sterile water, shaken and one cubic centimeter transferred to a sterile Petri dish by means of a sterile pipette. If the material is heavily infected, as it would be if visibly mildewed, the number of organisms transferred in this 1 cc. is probably so large that well isolated colonies will not form. Another 1 cc. portion is therefore transferred with another sterile 1 cc. pipette to a tube containing 9 cc. of sterile water (a dilution of 1-10) and a third cc. of 1-10 to a bottle containing 99 cc. of sterile water (1-100 dilution). Each of these dilutions is thoroughly shaken and 1 cc. of each put in a sterile Petri dish. In order to be certain of obtaining well isolated colonies, a further dilution is usually made by putting 1 cc. of the 1-100 dilution in a tube of 9 cc. of water thus giving a 1-1000 dilution. One cc. of this is likewise transferred to a Petri dish. Agar is now poured into the dishes and the water and agar mixed by gentle rotation. Obviously, very hot agar should not be used or it will kill the organisms. If the agar is allowed to cool before pouring until the bottle can be held comfortably against the cheek, it will remain liquid long enough to pour and there is no danger of killing any of the organisms. The pipettes are sterilized in a copper can (Fig. 24) and each is used only once and discarded to be resterilized.

Where bacteria are the organisms to be studied, ordinary nutrient agar should be used. If molds are sought, Czapek's agar is better. The plates are incubated, probably best at 30°C, and examined every 24 hours until growth appears. It will probably be found that the 1-1 and possibly several higher dilutions are completely overgrown. These plates must be discarded. If all plates are overgrown, the process must be repeated using higher dilutions. When a plate has been obtained which contains well separated colonies, a sample is "fished" (picked up on a platinum wire) and transferred to an agar slant for further work. It should be emphasized that nothing but round colonies well isolated from others (at least 3 mm) should be considered suitable for fishing. In fishing a mold, spores should be taken from the center of the colony and collected by gently brushing a platinum loop

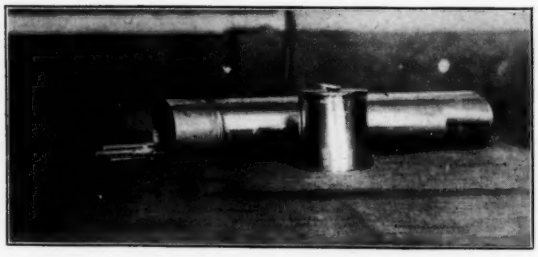

Figure 24.
Copper can for sterilizing pipettes.

containing sterile water over as few spore heads as possible.

This simple method works in most cases, but certain molds, particularly mucors, have a tendency to spread so fast that they may fill a plate before spore heads appear. Reducing the amount of nutrient in the agar will sometimes remedy this. A further difficulty may be encountered in separating slow growing molds from some bacteria. The molds grow so slowly that the whole plate is overgrown with bacteria before spores appear on the mold. Henrici[2] states that this condition can be corrected by making a sterile mixture of 50 grams of dextrose and 5 grams of tartaric acid in 100 cc. of water and adding this in the ratio of 1 cc. of the above solution to every 10 cc. of melted sterile agar. The mixture cannot be added before sterilization as the acid prevents solidification of the agar if so used. This mixture gives the medium an acid reaction a high sugar content. Both of these conditions hinder the growth of bacteria and promote mold growth.

The culture fished from the dilution plate is *probably* pure. It should be replated either by washing off a needle infected from the agar slant in sterile water, preparing dilutions, and plating; or by lightly infecting a needle and sweeping it back and forth over the surface of three sterile hardened plates, covering as long a path as possible without crossing the lines at any point. Figures 25 and 26 show such plates. The first (Fig. 25) represents conditions when the sweep is first started and organisms are plentiful on the needle, a continuous line of growth. Figure 26 shows conditions such as are obtained on the second and third plates, where most of the organisms have been wiped off and isolated colonies are found. The method is much better for bacteria than for molds. Isolated colonies falling outside the line of the needle are the result of accidental infection and should never be used. Such a colony is shown in one of the figures.

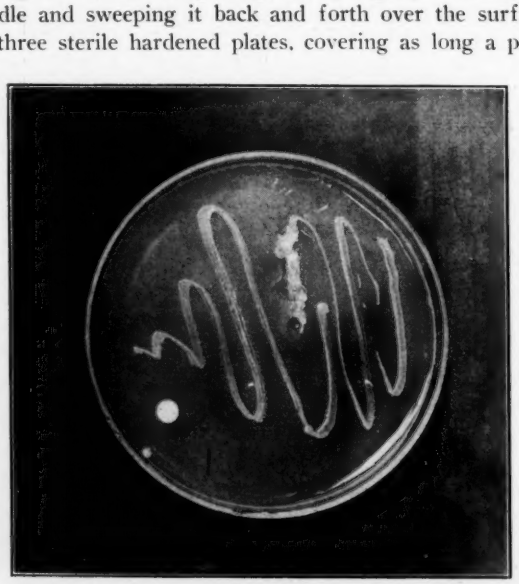

Figure 25.
Agar plate with solid line of growth. Note isolated colony due to accidental infection.

An easier but not so thorough method of getting the organisms off the material is to rub the infected portion over a Petri dish. This will probably not give isolated colonies, so further plating will be necessary to obtain pure cultures.

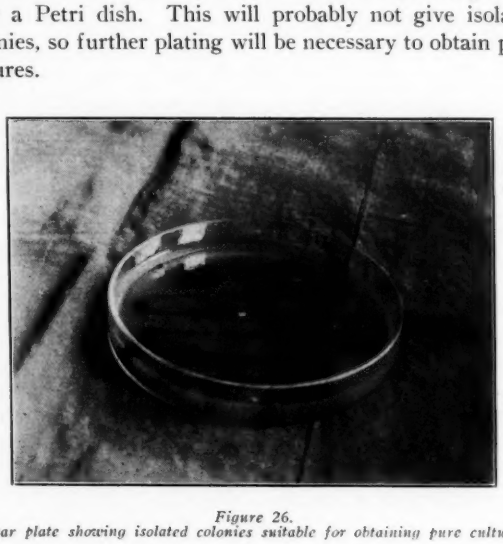

Figure 26.
Agar plate showing isolated colonies suitable for obtaining pure cultures.

A method recommended by Thom and Church[3] for obtaining pure cultures is to pick off a single spore head under a magnifying glass with sterile forceps, and put this spore head into an appropriate medium. The method is more difficult than it sounds.

Another valuable piece of information may be gained from these dilution plates. This is the relative number of organisms present in a sample. By counting all the colonies, some idea of the total number of organisms originally present in a sample may be gained, and a fair comparison of two samples made by using similar amounts of each. The American Public Health Association recommends counting the plate containing between 30 and 300 colonies and multiplying by the dilution. Of course, in textile work, the number of colonies recorded does not represent the total number of organisms originally present in the sample because even the most vigorous shaking will not transfer all the infection from the fibers to the liquid. However, for purposes of comparison a fair estimate of the total count may be made. It must be borne in mind that in making dilutions only 1/10 of the whole suspension was taken to make the 1-10 dilution so all numbers must be multiplied by 10 times the dilution in this case. A fairly accurate estimate of the relative num-

bers of two organisms may be made by this method if their colonies differ enough in appearance to make distinguishing between them sure. The greatest possibility of error arises through the differences in ease of growth of the two organisms on the medium used.

Besides the textile fibers themselves, there arises also occasionally the necessity of testing other materials around the mill, size baths for example. The testing of liquids of this nature is much easier than the testing of fibers because they may be plated and diluted directly, without suspending them in water. In these cases, of course, a true count may be obtained.

It is frequently desirable to know whether a persistent infection is being introduced from outside through the raw material or is present in the air of the mill. The infections of the air may be found by exposing Petri dishes to the air in the place to be tested until enough spores have collected to give a convenient growth. The time necessary can only be found by trial. Very dusty rooms may pick up enough infection in fifteen minutes or less, but a room which is quite free from dust may require several hours' exposure. By an examination of the colonies found on these plates from the air and comparison with those found on plates of the product and the raw material, a good idea of the source of the infection may be obtained.

Once the organism has been obtained in pure culture it is usually necessary next to identify it. Occasionally this step may be omitted and the culture tested directly by reinfection on sterile fiber. The preparation of large cultures for this purpose is easily carried out where small amounts of nutrient are not undesirable. They are prepared by slanting a bottle of agar and planting the organism generously over the surface (Fig. 27). This gives a very large number of organisms which may be washed off with sterile water and the suspension so formed used to infect cloth, yarn, or fiber. If small amounts of nutrient are apt to interfere with the test in question, this method is of little use because the water used to make the suspension always dissolves more or less of the agar. For a suspension in pure water, a bottle of broth is infected, given ample time to grow, and the organisms centrifuged out. The sediment is washed several times with sterile water, centrifuging the organisms out of each wash water. By increasing the number of washes, any degree of purity may be obtained in the final suspension. Increasing the number of washes increases the chances of air born infection in the pure culture so extreme precautions must be exercised.

Figure 27.
Agar slanted in bottle to give very large surface for growth.

The sterilization of textile materials presents a real problem. Heat treatment, particularly of wool and silk, probably changes the constitution of the surface at least of the fibers treated. If any treatment does cause changes, tests run on sterilized materials will not be comparable with actual conditions. Careful investigation of this part of microbiological work should certainly be made, but none has so far been published. The worker must therefore use his own judgment. For sterilizing cotton, the author has used steam at atmospheric pressure. Probably even this is too drastic for wool, which is dissolved by hot water alone. Silk is also delicate and it is a well known fact that any dyeing process on silk must be complete in one-half hour as the water exerts a destructive action. For sensitive tests with micro-organisms this is obviously too strong a treatment. Here is a real problem for the textile chemist. The microbiologist must work with sterile materials; what method may be used which will effect complete sterilization yet have no action on the fiber?

News Item

Mr. R. W. Philip, Editor of "Cotton," recently gave a very worth while and instructive talk to the textile students of the Clemson Textile Department. His subject was "The College Man in the Mill."

Hosiery Card

Nine new colors will be portrayed in the 1932 Spring Hosiery Card now in preparation, it was announced recently by Margaret Hayden Rorke, managing director of the Textile Color Card Association. Advance swatches of these shades were recently sent out to members in the hosiery industry.

The Spring hosiery tones have been especially chosen because of their smart harmonizing or contrasting qualities with the fashionable shades in textiles, garments and shoes for the coming season, thus assuring correct color coordination in the ensemble.

The 1932 Spring Hosiery Card, which will be issued shortly, will be accompanied by a printed chart in which the new hosiery colors will be correlated with the official shoe and leather colors for Spring 1932.

Held Sales Convention

American Aniline Products, Inc., held its annual sales convention Dec. 21st and 22nd. The meeting was held at Lock Haven, Pa. where their principal factory, for the production of dyestuff, is located. The entire sales force was present in addition to the executives of the Company. The salesmen were agreeably surprised to note the tremendous change and improvements which have taken place recently. The two new large modern and concrete buildings were especially noted. At the dinner held on Monday evening Dec. 21st, attended not only by the entire visiting group but by the heads of departments of the plant, a great tribute was paid to the Works manager by the president Mr. B. R. Armour. The entire details for the meeting were directed by Mr. G. L. Armour who presided over the meeting.

The Term Rayon

The term silk must no longer be used to describe rayon in Spain. In accordance with a decree just issued by the Ministry of National Economy of Spain, it has been ruled that some name must be adopted by Spanish producers and distributors of the so-called synthetic textile fibers which does not in any way contain the word silk. The purpose of this decree has been to protect the silk industry of the country and also the consumer in their purchases of real silk products. It seems quite probable that the term rayon will be adopted.

From another news item it is learned that the word silk alone, or in combination, must be applied exclusively to the products of the silk worm in accordance with a Bill which is being prepared by the Italian Government through their Department of Commerce. Up to the present time the term artificial silk has been quite generally used in Italy. The term rayon was at first rejected, but according to the *Daily News Record*, it now appears highly probably that rayon will be adopted by the Italian trade.

Japanese Dye Imports Increase

Imports of coal-tar dyes into Japan showed a radical increase during the first three quarters of 1931, of almost a million pounds. In coming shipments during this period amounted to 3,431,981 pounds, compared with 2,437,145 pounds during the 1930 three quarter period. During this period indigo replaced the direct cotton colors as the most important type of dye imported, on the basis of quantity, but not value, and accounting for 300,000 pounds of the increase.

New Homogeneous Dye

The General Dyestuff Corporation releases a new homogeneous dyestuff under the name of Indanthren Orange 7RK. This new dyestuff is recommended by the manufacturer for dyeing cotton, linen and other vegetable fibres.

As regards shade Indanthren Orange 7RK is slightly redder than Indanthren Orange 6RTK, over which it is said to have the advantage of a greater tinctorial strength and a brighter shade.

Indanthren Orange 7RK is claimed to have excellent fastness to washing, boiling and chlorine and very good fastness to peroxide and boiling soda.

New Consulting Firm

Announcement was made recently of the formation of a new consulting firm to be known as Hathorne & Green. They have offices at 114 East 32nd Street. They will specialize in rayon. The partners are Berekeley L. Hathorne and Henry Green, formerly of the Tubize Chatillon Corporation. They will continue to serve this organization in a consulting capacity.

British Dye Exports Increase

British exports of coal-tar dyes during the first ten months of 1931 amounting to 98,584 hundredweight, worth £844,840 were a considerable increase over the 92,757 hundredweight, valued at £747,110 shipped during the 1930 ten-month period.

New Suprafix Dye

The General Dyestuff Corporation releases Indanthren Printing Blue GG Suprafix a valuable addition to the range of the Suprafix Dyestuffs.

This new Vat Blue is said to fix very easily in ageing and to possess excellent fastness to chlorine, in which respect it is said to excel any Vat Blue of similar shade in existence.

The manufacturer claims that this color can also be used for dyeing and discharges to a pure white with Rongalite CL.

Alkaline Builders Compared

The above is the title of a new booklet distributed by the Cowles Detergent Co. of Cleveland, Ohio.

The booklet is claimed to be both very complete and timely because business conditions which have prevailed during the past two years have prompted the introduction of inferior goods into every market, and the builder market has experienced its full share of misuse in that respect.

Services offered by the company are having a field man keep your plant tuned up and also the information issued periodically by the Cowles Technical Service Laboratories.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

POSITION WANTED

Textile Chemist and Colorist with ten years' practical experience, being available, solicits inquiries. Address Box No. 710, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

POSITION WANTED

Chemist-dyer, cotton all forms, rayon. All classes dyes. Fifteen years' experience. Capable of bleaching, dyeing various fibers and producing results. Location immaterial. Reasonable salary. Address Box No. 715, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

POSITION WANTED

Industrial Chemist with sixteen years' practical experience dyeing and printing textiles and testing dyestuffs and finished piece goods, knit goods, etc., wishes position in plant or testing laboratory. Available immediately. Address Box No. 716, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.